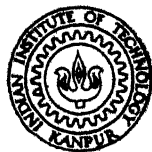


SINTERED MULLITE

By

S. VENKATARAMANI



INTERDISCIPLINARY PROGRAMME IN MATERIALS SCIENCE

INDIAN INSTITUTE OF TECHNOLOGY KANPUR

AUGUST, 1975

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SINTERED MULLITE

**A Thesis Submitted
in partial Fulfilment of the Requirements
for the Degree of
MASTER OF TECHNOLOGY**

**By
S. VENKATARAMANI**

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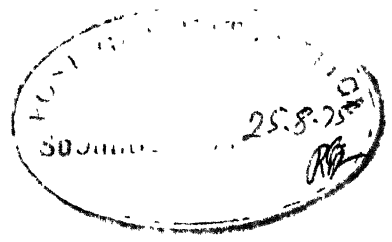
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<p>POST GRADUATE OFFICE</p> <p>This thesis has been approved for the award of the Degree of Master of Technology (M.Tech.) in accordance with the regulations of the Indian Institute of Technology Kanpur Dated. 25.8.73</p>

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SYNOPSIS

This investigation is concerned with the preparation of sintered mullite from clay alumina mixtures. The source and characteristics of raw materials, the role of mineralizers and the process parameters were examined.

Chapter 1 presents a detailed review of the structure and properties of mullite, phase relationships in the $\text{Al}_2\text{O}_3 - \text{SiO}_2$ system and its synthesis from the various raw materials with and without the additives.

The objectives of the present work are set forth in Chapter 2 as the investigations of the effects of clay/alumina ratio, different sources of alumina, sintering temperature and time, and amounts of different additives on the formation of mullite.

The various experimental procedures adopted for the preparation of sintered mullite and for its characterization are given in Chapter 3. The characteristics of the raw materials, the ratios of the various starting materials, mixing, moulding and sintering, are included followed by the measurement of shrinkage, density, porosity, X-ray phase analysis, chemical analysis, microstructure and modulus of rupture.

Chapter 4 summarises the main results of the investigation together with interpretations. It was found necessary to make the clay/alumina mix poorer in alumina than the stoichiometric ratio to obtain maximum mullitization. This is attributed to loss of SiO_2 during sintering. Alcoa A = 2 alumina and Malco alumina were nearly equally satisfactory but substitution of these in part or full by finer grained alumina such as A = 16 Alcoa and Hydral 710 was found beneficial. The mineralizers chosen from available literature lead to a positive conclusion about FeO , MnO_2 , CuO , MgO , ZnO and CaO as effective mineralizers. The optimum amount however varied and was also a function of sintering conditions. The factors which influence the effectiveness of the mineralizers were identified as the tendency for liquid formation and the tendency for the creation of point defects.

CHAPTER 1

INTRODUCTION

1.1 GENERAL:

The Aluminosilicate refractories are one of the most important and widely used of the various types of refractories. The important constituent of the aluminosilicate refractory is Mullite, usually known as an aluminosilicate of the chemical formula $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$. It, however, has a composition range from $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ to approximately $2\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$, existing as a solid solution between these composition limits.

Mullite is the only stable crystalline compound in the $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ system under normal atmospheric pressure. The other more common natural aluminosilicates namely Andalusite, Sillimanite and Kyanite transform into mullite at high temperatures characteristic to their respective transformations.

Mullite is very rarely a natural material, the most important place of its occurrence being the Isle of Mull, Scotland, from which it derives its name. It, however, is one of the most common phases found in the artificial industrial ceramic products. Porcelain, fire-clay products, high alumina refractories etc. contain

mullite as one of their important constituents. In all these products mullite is normally formed in situ except in certain products where either fused or sintered Mullite is used as one of the raw materials. Because of its excellent mechanical, chemical, thermal and electrical properties, it has a wide range of applications extending from super refractories to substrates in the electronic industry.

Mullite normally crystallises in the orthorhombic system in the acicular form or as elongated needles except when it is prepared in the absence of a liquid phase under which conditions the crystallites are usually globular.

Mullite is made in a large scale by the electric arc fusion method. This involves arc melting of the raw materials - aluminosilicates, alumina and silica - at about 2000°C plus and cooling the melt at controlled rates to produce needle shaped mullite crystals. The purest mullite is white in colour and depending on the amount of impurities the colour varies from grey to black. The main impurities that impart colour are the oxides of iron and titanium. A fairly large quantity of mullite is made, also by sintering, the concerned raw materials. The raw materials here are necessarily fine powders of a few microns size. They are blended, briquetted or formed into any other shape required and fired at nearly the

melting point 1810°C , preferably at a couple of hundred degrees less so that liquid formation or vitrification is avoided. This method is more commonly used for making ceramic wares where mullite is formed in situ. The crystal size and shape largely depend on the temperature of sintering, soaking period, rate of cooling and addition of mineralizers, if any.

1.2 THE Al_2O_3 - SiO_2 SYSTEM:

The Al_2O_3 - SiO_2 system is still the most important binary system in the field of refractories. Detailed research has been carried out for nearly half a century but however there have been conflicting ideas regarding the exact nature of the system especially in the mullite region. Hence it is still difficult for those who use this system to come to any definite conclusion regarding the correct interpretation.

The first investigators of the system Al_2O_3 - SiO_2 , Shepherd, Rankine and Wright¹ (1909) described 'Sillimanite' as the sole crystalline compound of the system, having a congruent melting point at $1811 \pm 10^{\circ}\text{C}$. The eutectic composition between 'Sillimanite' and cristobalite contain 10 percent Al_2O_3 with its melting point at 1600°C . Although according to Beckman (1902) the refractive index of the artificial sillimanite is less than that of the natural

mineral, the study of Shepherd and coworkers does not explain this. Later, their investigations were confirmed by Shepherd and Rankin^{2,3} (1911,1915) with the determination of the same eutectic points, modifying only some temperature data. Shepherd et al¹ visualised a vitreous phase in the inclusions in the 'Sillimanite' and named it as 'Sillimanite glass' having a refractive index, $n_D = 1.530$. This was very soon discredited by the fact that 'Sillimanite' has such a crystallisation ability that it never remains in a vitreous state even if the melt is quenched most rapidly and consequently the glass can not be 'sillimanite glass'.

Later on the investigations by Bowen and Greig⁴ and the phase diagram published by them have changed all the theories regarding this problem. They showed a crystalline solid, 'Mullite' of a composition $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ (71.8 wt % Al_2O_3) to melt incongruently at 1810°C and identical with natural mullite. They had used a static method of investigating with mixes of pure synthetic alumine and silica as well as natural mineral sillimanite. The raw materials were mixed in different ratios and fused in air atmosphere and quenched in a suitable coolant. The phase diagram (fig. 1.1) published by them, has been criticised for a long time, but its main statement - 'MULLITE is the only stable crystalline compound' - is accepted even today.

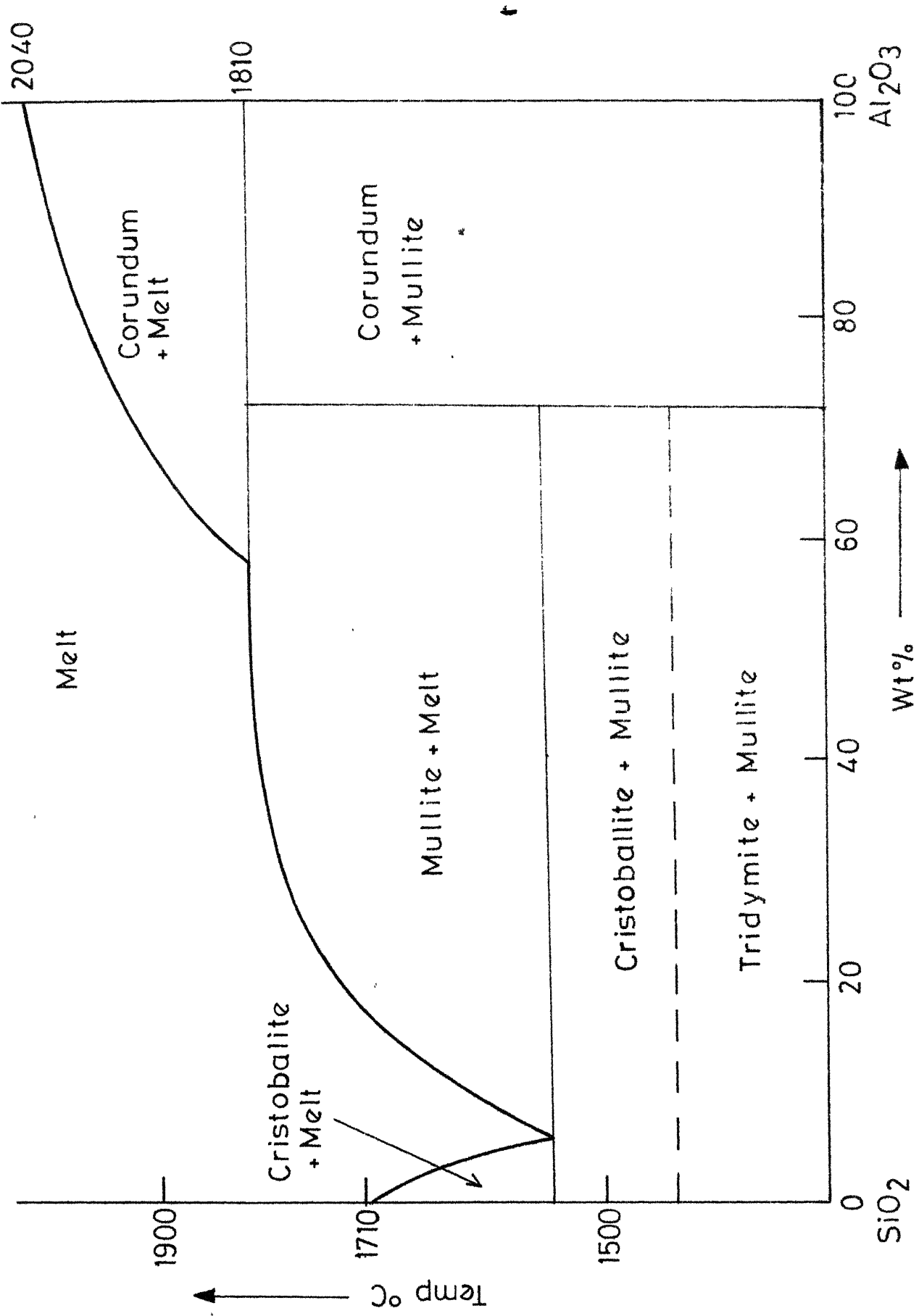


FIG.1.1 THE SYSTEM Al_2O_3 - SiO_2 (Bowen & Greig (1924) Ref.....4)

The other important features of their phase diagram are (i) The eutectic invariant between SiO_2 and Mullite contains 5.5 Al_2O_3 , (ii) There is no eutectic between Al_2O_3 and mullite, but there is a reaction (peritectic) invariant point and (iii) System Al_2O_3 - SiO_2 contains only one liquid phase and there is no liquid segregation.

Morris⁵ has modified some characteristic temperatures of this system. According to him the eutectic point between silica and mullite is at 1551°C , the melting points of mullite, cristobalite and corundum are respectively 1827 , 1729 and 2083°C .

Later on, Bauer et al⁶ succeeded in producing single crystals of mullite by flame fusion technique. They avoided the incongruent melting region by quenching the melt with a steep thermal gradient so that the crystallisation occurred at 1830°C whereas the fused surface was at 1930°C . Thus alumina was not allowed to get into equilibrium with the melt. However single crystal growth is not a usual occurrence in incongruently melting materials. This raised the question of congruent melting of the mullite. Moreover the volatilisation of silica from sillimanite melt or any other artificial aluminosilicate melt has been observed. This enriches the melt with alumina, the melt finally reaching the composition of mullite. This phenomenon also explains the flattening of the liquidus

curve of the phase diagram proposed by Bowen and Greig¹ (fig. 1.1) from the 5.5% alumina eutectic towards the alumina side.

Toropov and Galakhov⁷ were the first to emphasise the importance of silica evaporation and put forward a different conception of the melting behaviour of mullite (fig. 1.2). A mixture of alumina gel and quartz covered with a thin tungsten film to prevent evaporation of silica when heated in a tungsten wound microfurnace in high vacuum, the mullite compound melted without decomposing i.e. CONGRUENTLY. This consequently showed up a second eutectic between corundum and mullite at 77.5% Al_2O_3 and 1945°C. Further examinations by Budinkov et al⁸ by DTA of the high alumina side of the phase diagram confirmed the congruent melting of mullite (77% Al_2O_3). The melting point determined was $1900 \pm 20^\circ\text{C}$. A careful X-ray study of the 77% Al_2O_3 mix undoubtedly showed the congruent character of mullite melting. On the other hand in the same year Filonenko and his coworker⁹, also using DTA established that mullite crystals which were embedded in glass decomposed above 1820°C into corundum and a silica rich melt and therefore mullite had an incongruent melting behaviour.

It was Posnjak and Greig¹⁰ who first presumed the solid solution of Alumina in the mullite lattice. This was corroborated later by the experiments of Sosmon¹¹.

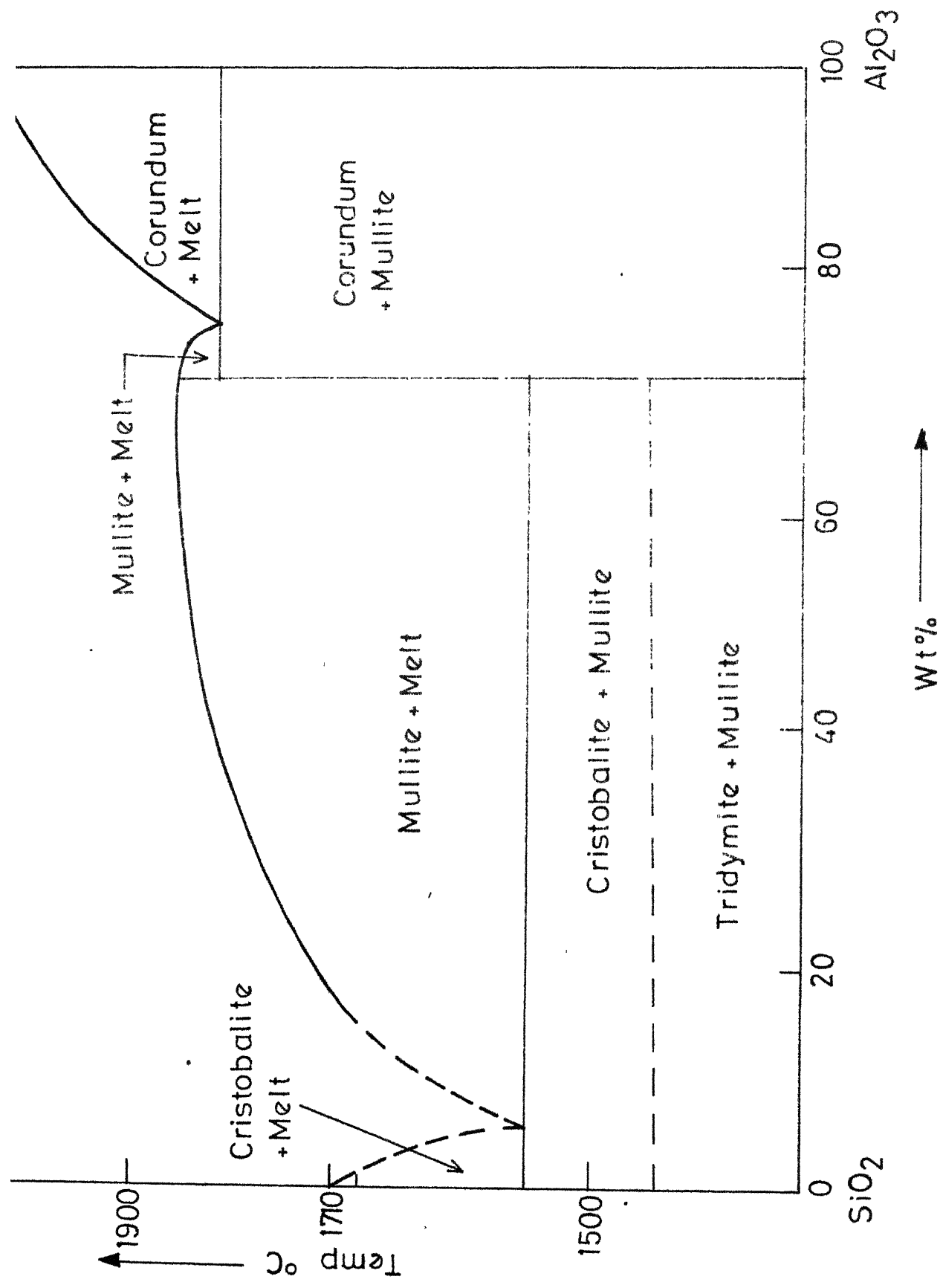


FIG.1.2 THE SYSTEM Al_2O_3 - SiO_2 (Toropov & Gaiahnov (1951) Ref.7)

It has been more cautiously stated by Posnjak and Greig that mullite can take alumina in the form of a solid solution to a limit of $75\% \text{Al}_2\text{O}_3$ (i.e. a quantity 3% higher than the theoretical $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$). This is accomplished by an expansion of the mullite lattice which has been detected by X-ray diffraction. Following this, many authors e.g. Rocksby and Partridge¹², Bouta and Barta¹³, Neuhaus and Richartz¹⁴ have confirmed that solid solutions can form between mullite and corundum. Accordingly, Shears and Archibald¹⁵ after a study of the available literature proposed a composition range for mullite in the diagram of Boven and Greigl (fig. 1.3).

The investigations of Tromel et al¹⁶ also contributed to the finding that mullite can exist in an higher alumina silica ratio than 3:2. and that it melts incongruently at 1820°C . The differences in opinion in the melting of mullite has been traced to the differences in the heating and cooling schedules used by the various investigators. Their results indicated that no corundum was seen if the melting was complete in short runs (1-2 hrs), but increasing the duration of heating (4 hrs) caused the appearance of corundum. Hence Tromel concluded that congruent melting occurs when the samples were kept at high temperature only for a short time like in the case of experiments by Toropov et al and in growing of single

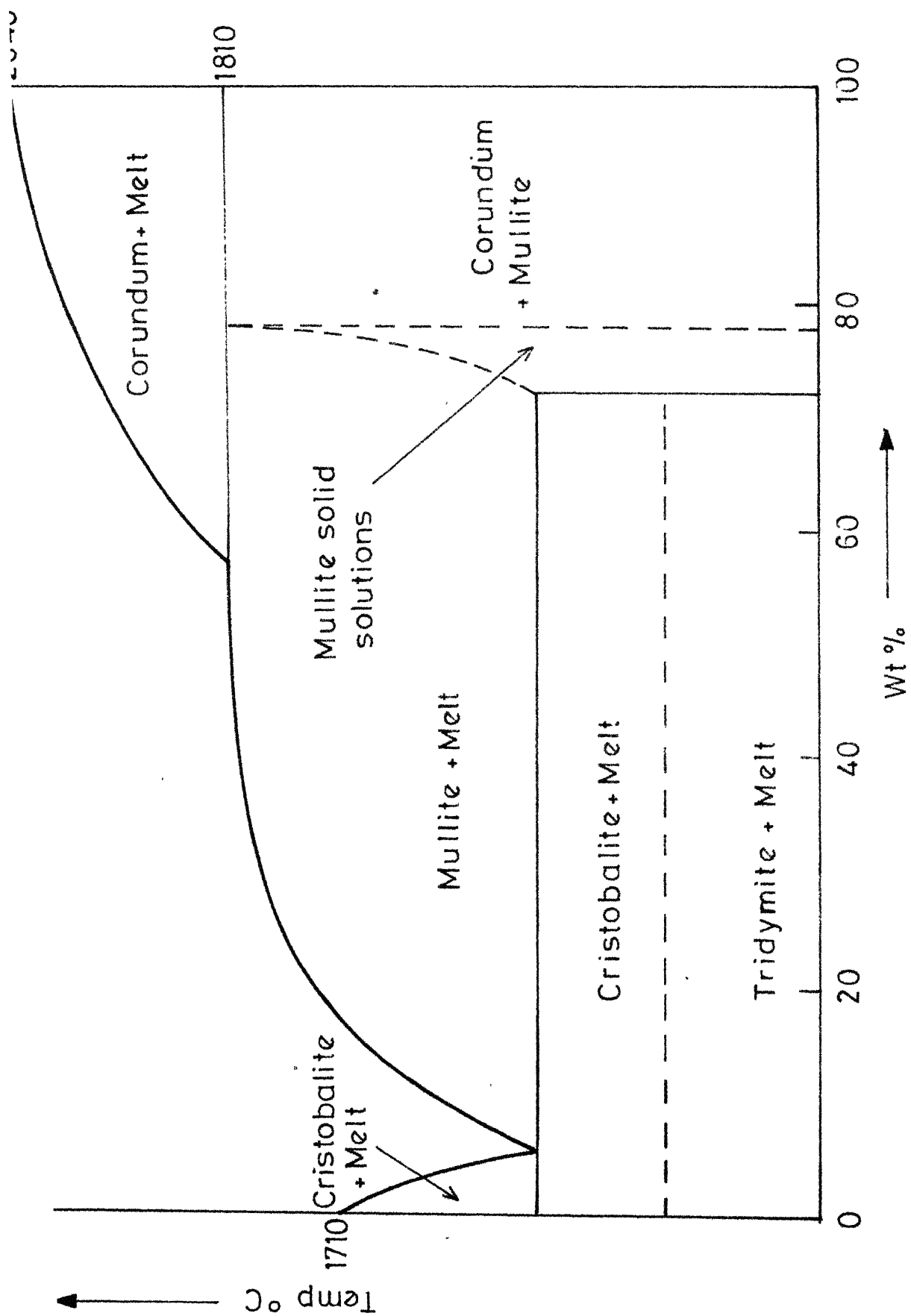


FIG. 1.3 THE SYSTEM Al_2O_3 - SiO_2 (Shears & Archibald (1954) Ref....15)

crystals. On the other hand, in the case of prolonged firings mullite melts incongruently. This has been attributed to the slower diffusion process connected with the precipitation of corundum from the melt in the composition range from 54 to 77% Al_2O_3 relative to that of mullite.

Toropov and Galakhov¹⁷ in 1958 in an effort to put an end to this problem again experimented. Quenching was used and samples were analysed both by optical microscopy and X-ray diffraction techniques. The later diagram (fig. 1.4) shows the presence of a solid-solution between mullite and corundum from $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ to $2\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ and the eutectic between mullite and corundum at 79% Al_2O_3 and 1850°C.

Due to the rapid crystallization during quenching, negligible amount of glass was formed. But the tiny secondary crystals thus formed were undoubtedly distinguishable from the big primary crystals formed during the thermal exposition slightly below the liquidus. Since the rapid crystallization of the residuary melt is in equilibrium with the solid phase, the determination of the solidus line, shown as dotted line in fig. 1.4 is not very exact.

The congruent melting behaviour of Mullite was again questioned by Welch¹⁸. He added strength to the

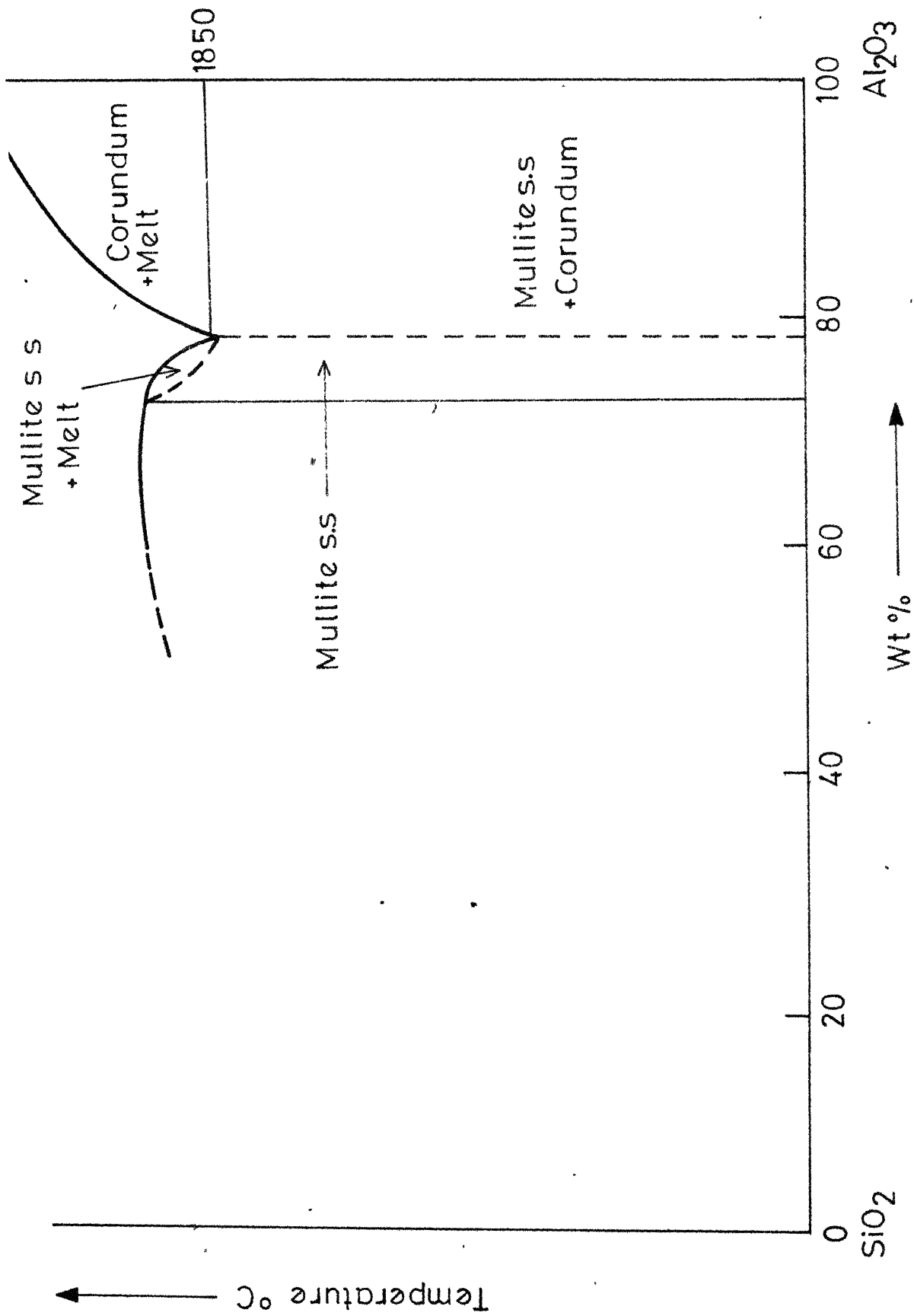


FIG. 1.4 PART OF THE SYSTEM Al_2O_3 - SiO_2 (Toropov & Galakhov (1958) Ref....17)

arguments for the incongruent melting behaviour through direct observations of the melting of mullite with a high temperature microscope and investigations of the cooling curves for the solidus and liquidus of corundum and liquidus of mullite. Accordingly, though the primary area of mullite contains the composition $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, this compound has no significance. Moreover, Mullite is just one member of the vast series of solid-solution from $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ to $2\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$. In conclusion the area of solid solution extends to an alumina content of 75% by wt. and mullite melts incongruently at 1880°C .

It was Aramaki and Roy¹⁹ who rather convincingly solved the mullite problem. They had eliminated all the previous objections in experimental techniques and also had critically compared the results of the important investigations with their own. Samples prepared from gels were used for subsolidus work and a mixture of dry $\alpha\text{-Al}_2\text{O}_3$ and powdered silica glass was used in the region above the solidus curve. The runs were carried out in sealed noble metal containers and the melt was cooled using quench technique.

On comparing their findings with the results and conclusions of the earlier investigators, the authors differed with Neuhaus and Richartz¹⁴, Bauer et al⁶ and Barta and Barta¹³ in that the latter did not observed a

substantial amount ($\sim 50\%$) of corundum which must exist when a $2\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ composition melts incongruently. On the point of silica evaporation the authors argue that none of the earlier investigators had an exact idea of the role of silica evaporation. It is also argued that silica must evaporate much faster from the melt than from the solid body and hence it is important to see whether the sample had melted or not. Also, the presence of hydrogen in some of the previous investigations (Rooksby and Patridge¹² and Barta and Barta¹³) reaching to form water, and hence causing the formation of more volatile SiO_2 should have influenced the volatilization of SiO_2 . While discussing in detail about the formation of glass reported by Trömel et al¹⁶ (1958) it was opined that it is a remote probability that glass would form in the composition range from 60% to $70\% \text{Al}_2\text{O}_3$ under the very slow cooling conditions employed by Tromel et al¹⁶ (1958). Moreover there has been no exact statements about the amount of corundum formed and also there exists a possibility of silica evaporation and hence corundum formation at the surface layers. Also, Roy refutes Trömel's hypothesis for the slow precipitation of corundum by the argument that, it forms easily when it is the equilibrium phase. The phase diagram for the Al_2O_3 - SiO_2 system, thus proposed after a detailed discussion and

a critical review of the earlier work combined with the results of the investigations (fig. 1.5) reveals that mullite melts congruently at 1850°C . The solid solution of Al_2O_3 in mullite extends from ~ 71.8 (3:2 ratio) to $74.3\% \text{Al}_2\text{O}_3$. There is however a possibility of the preparation of a metastable solid solution from the melt up to $77.3\% \text{Al}_2\text{O}_3$ (2:1 ratio). Silica, according to the observations is not soluble in mullite below the 3:2 composition at normal pressures.

Though the congruent melting behaviour of mullite has again been questioned by Horibe and Kuwabara²⁰ based on their detailed direct observation of melting of mullite combined with X-ray investigations, the results of Aramaki and Roy has been recently confirmed by Rehfeld and Schwiete²¹. The X-ray and microscopic examination of Al_2O_3 72-80% and silica 28-20% by weight and also the compositions of 2:1 and 3:2 mole ratios of Al_2O_3 and SiO_2 after heating at $1820-1970^{\circ}\text{C}$, fully exposed to air and soaked for at least 40 minutes, revealed that mullite melts only congruently irrespective of whether the melt is quenched or slowly cooled. The presence of corundum was observed only if Al_2O_3 to SiO_2 ratio was greater than 2 to 1.

A recent comprehensive investigation by Pask et al²² using diffusion couple experiments and static

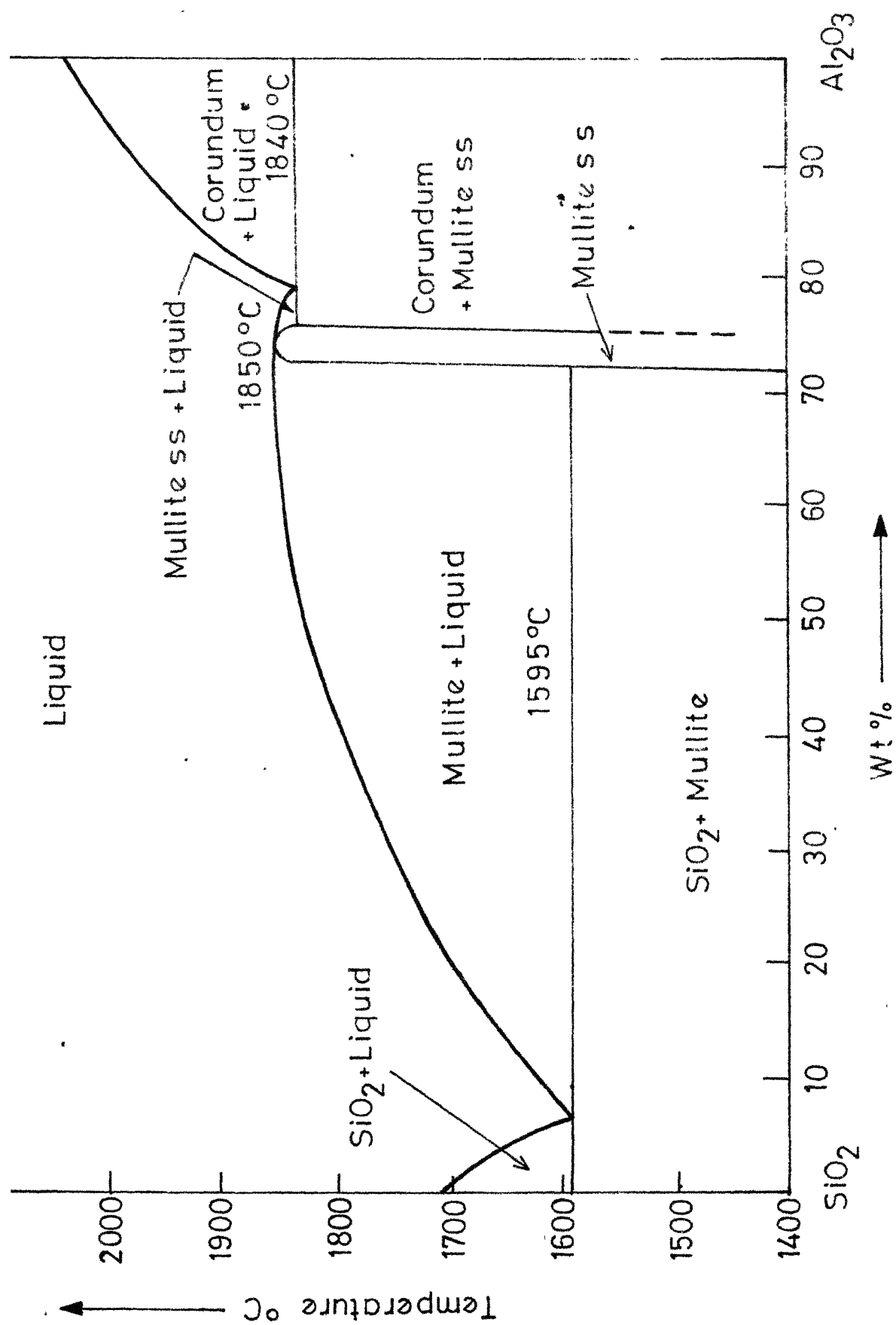


FIG.1.5 THE SYSTEM Al_2O_3 - SiO_2 (Aramaki and Roy (1962) Ref ...19)

method of quenching has revealed certain facts which are quite relevant. The facts are (1) mullite melts incongruently to form a silica rich liquid and a solid Al_2O_3 phase, the stable mullite field lying below 1853°C . The incongruent melting point of mullite is observed to be $1828 \pm 10^\circ\text{C}$ from the intersection of the extrapolated liquidus lines of mullite and Al_2O_3 and (2) the solid solution range extends between 70.5 to 74.0 percent alumina and corresponds to a nominal composition of $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$. However their static quenching techniques agreed with the earlier results of Bauer et al. Higher Al_2O_3 solid solutions ($>74\% \text{Al}_2\text{O}_3$) can be formed only when precipitated from a melt. The latest representation of the Al_2O_3 - SiO_2 system is given in fig. 1.6.

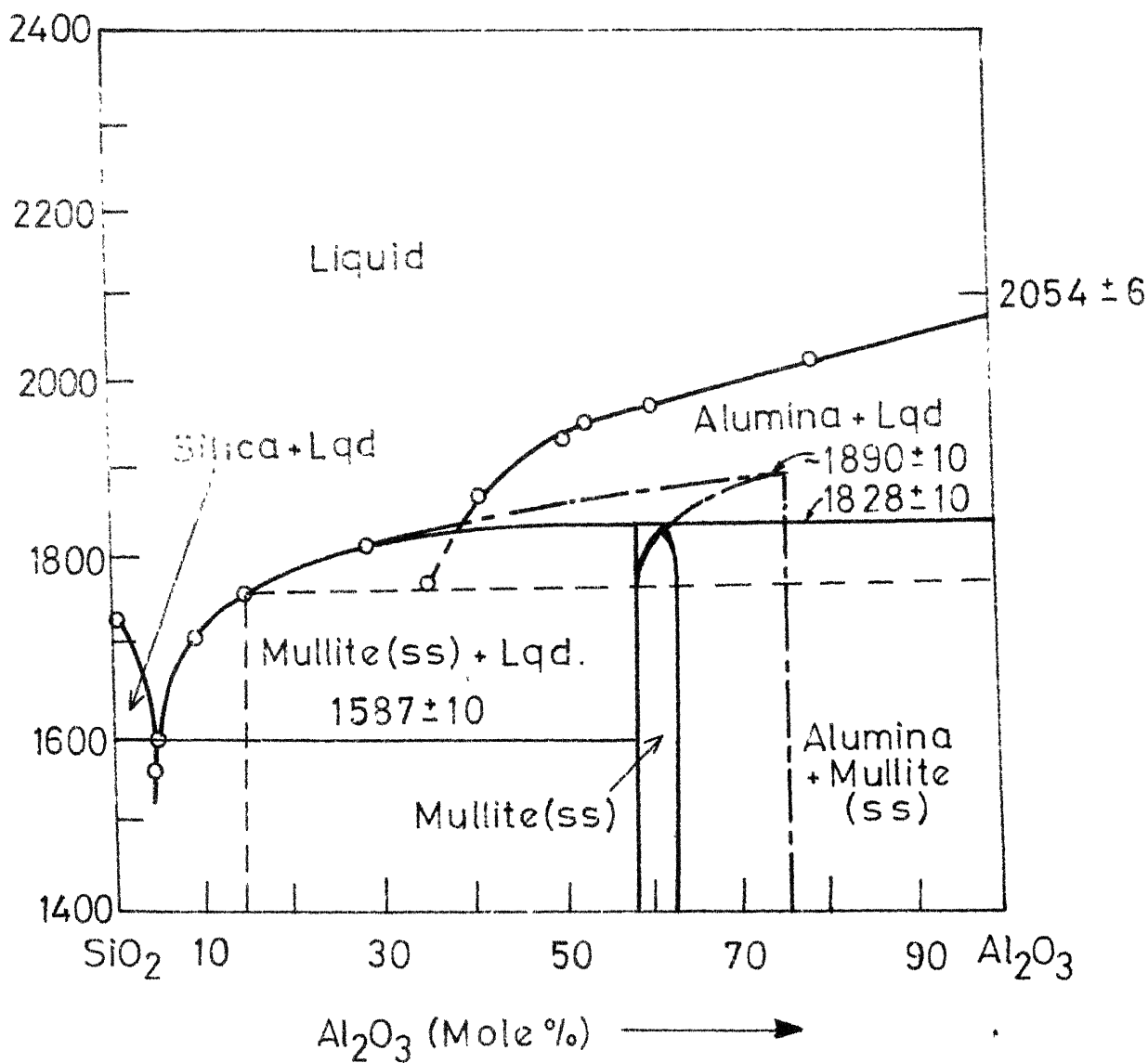
1.3 CRYSTAL STRUCTURES OF MULLITE AND SILLIMANITE AND THEIR RELATIONSHIP:

Mullite falls in the orthorhombic system of crystals. The crystals are usually acicular in shape. The structural properties of the aluminosilicates are given in Table 1.1. The basic unit cell consists of 12 Si, 36 Al and 78 oxygen ions. The cell dimensions of mullite are

$$a = 7.584 \pm 0.003 \text{ \AA}$$

$$b = 7.693 \pm 0.003 \text{ \AA}$$

$$c = 2.890 \pm 0.001 \text{ \AA}$$



6 Al_2O_3 - SiO_2 SYSTEM (Pasketal Ref....22)

Table 1.1: Some Properties of Alumino Silicates

Formula	Sillimanite		Andalusite		Kyanite		Mullite	
	$\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$		$\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$		$\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$		$3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$	
Specific gravity g ml^{-1}	3.08		3.18		3.59		3.03	
Hardness Mohs	7.5		7.5		Changing		7.5	
Index of refraction	1.66		1.65		1.75		1.65	
Birefringence	0.022		0.010		0.011		0.012	
Crystal system	Orthorhombic		Orthorhombic		Triclinic		Orthorhombic	
Crystal habit	Fibrous		Prismatic		Plates		Acicular	
Positions and intensities of three strongest X-ray reflections	$d, \text{\AA}$	I	$d, \text{\AA}$	I	$d, \text{\AA}$	I	$d, \text{\AA}$	I
	3.36	1.00	4.58	100	3.18	100	3.39	100
	3.40	1.00	1.48	100	1.93	75	3.43	95
	2.20	.90	2.17	80	1.37	50	2.21	60

The unit cell volume is $168.61 \pm 20 \text{ \AA}^3$ Mullite has got a striking resemblance to sillimanite from the structural point of view and in fact on the basis of X-ray diffraction patterns (ref. Table 1.1) it is almost indistinguishable from sillimanite which is of the composition $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ and stable at high temperatures and pressures.

There are other forms of mullite apart from the α -mullite - $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ - reported in the literature. They are (1) β -mullite¹² which is essentially $2\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ and incidentally has excess of alumina in solid solution. (2) γ -mullite¹² - having small amounts of iron oxide or titanium oxide in solid solution. These have been characterised by the distinguishable differences in the axial ratios of the unit cells and the lattice expansion when the inclusions as the solid solutions are made. The β and γ forms can be synthesised and the natural mullite is largely one of these forms. Agrell and Smith²³ have reported a new so-called 'S' mullite. The existence of the various forms of mullite has been confirmed later by various investigators.

The other important aluminosilicates, sillimanite, kyanite and andalusite, though have the same chemical formula, $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$, are structurally quite different from each other.

There has been quite a lot of study of the structures of sillimanite and mullite and various relationships have been suggested. Basically,²⁴ the sillimanite structure (fig. 1.7) consists of chains of slightly distorted Al-O octahedra which run parallel to C-axis. These are supported by double chains of Al-O and Si-O tetrahedra in which the distribution of the Al and Si atoms are ordered. Each double chain may be construed as a continuous series of four-membered rings, with each ring containing two Si and two Al tetrahedra in the sequence Si-Al-Si-Al. The Si-O_C-Al₂ bond angle of 171.6° and the Si-O_D-Al₂ bond angle of 114.4° control the basic configuration of the ring. The O-Si-O tetrahedral angles are nearly ideal (107.40 - 111.3°) whereas the aluminium tetrahedron is more irregular. But in both cases the cations are displaced from the centre of their tetrahedra toward O_C.

Sadanaga et al²⁵ found that the unit cell of synthetic mullite of composition $2\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ contained 6/5 of the formula unit i.e. $\text{Al}_{4.8}\text{Si}_{1.2}\text{O}_{9.6}$, and is almost identical with sillimanite except that the C-axis is half the length of the sillimanite cell. Since a corresponding volume of sillimanite is $\text{Al}_4\text{Si}_2\text{O}_{10}$ they confirmed that while both structures have same number of cations per similar volume, the mullite is short of oxygen.

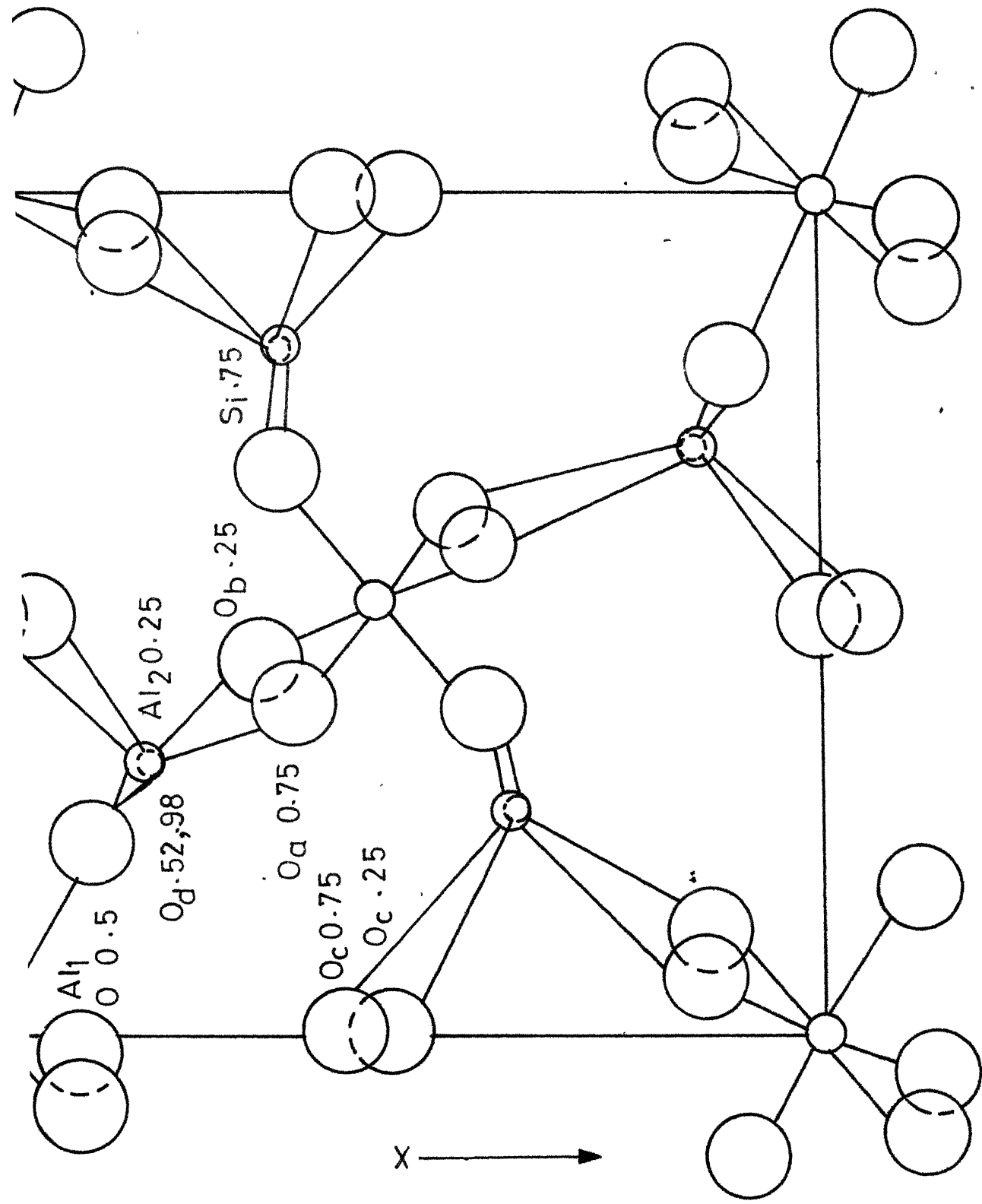


FIG.1.7 PROJECTION ON (001) OF THE REFINED STRUCTURE OF SILLIMANITE

(Ref.. 24)

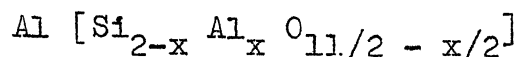
The defect mullite structure (fig. 1.8) is thus derived from that of sillimanite by replacing 0.8 silicon atom per sillimanite unit cell by 0.8 aluminium atom at random and removing 0.4 two coordinated oxygen atoms (O_C). Furthermore, with the loss of oxygen atoms 20 percent of the tetrahedral cation positions become incapable of being occupied. The new tetrahedral sites, previously unfilled in sillimanite, occupied by the 0.8 aluminium atom that had been forced out of the normal tetrahedral site require coordination to the oxygens O_C and hence these O_C are shifted slightly to O_C^* . The movement of the cations to the Al_2^* sites interrupts the continuous double tetrahedral chains of the original sillimanite.

Durovic²⁶ has proposed a similar structure for a synthetic mullite of $1.71 Al_2O_3 \cdot SiO_2$ composition. However, he has concluded that all the oxygen atoms whether O_C are O_C^* , are statistically distributed on either side of the symmetry centre at $1/2, 0, 1/2$ and that the new cation sites contain both aluminium and silicon atoms at random.

The controversy over the distribution of the aluminium and silicon atoms in the tetrahedral sites and the spatial distribution and positions of atoms in the incompletely filled O_C sites was eliminated by Burnham²⁷ in his extensive investigations. The refined structure thus proposed agrees mostly with the one proposed by

Sadanaga et al²⁴ (fig. 1.8). Based on the high resolution electron density plots it has been proposed that there are some oxygen nuclei present at the O_C^* sites and if the remaining oxygens were all distributed on O_C^* sites, as proposed by Durovic²⁵, then the maximum electron density would not occur around O_C as has been observed. The question concerning the occupation of Al_2^* site still remains unanswered. The refinements of the cation-anion distances though suggest that it preferentially contains aluminium atoms, other structural aspects indicate the presence of silicon atoms also.

Each of these investigators has considered the possibility of a continuous solid solution series from sillimanite to 2:1 mullite. Durovic has suggested a general formula as



where $1.25 \leq x \leq 1.40$ for mullites in the range 3:2 to 2:1.

However there has been no confirmation from experimental results on the possibility of a solid solution series from sillimanite to 2:1 mullite. The isomorphic replacement of silica by alumina in the sillimanite lattice, for obtaining a mullite structure is thus a proven fact.

1.4 FORMATION OF MULLITE

The aluminosilicates, aluminium hydrosilicates, artificial mixtures of alumina and silica and mixed gels of alumina and silica all transform into mullite at a high temperature. The reaction may be either slow or rapid, made up of one or more steps but the ultimate product is always mullite.

1.4.1 FROM Al_2SiO_5 ALUMINO SILICATES

The earliest studies of the transformation of the three aluminosilicates, kyanite, sillimanite and andalusite, were done by Norton²⁸ and Greig^{28a}. The transformations were observed microscopically and by volume change measurements during firing at systematically chosen temperatures. The conclusion is that kyanite transforms the most easily; traces of mullite showing up even at 1200°C. Mullite transformation is more rapid at higher temperatures and a silicious glass is a co-product. The observed exothermic effect at 1400°C when kyanite is heated is more probably due to recrystallisation than due to mullite formation.

Sillimanite also transforms into mullite after heating at 1550°C (at nearly the eutectic temperature of the Al_2O_3 - SiO_2 system). There has been no observance of any thermal effect.

Andalusite transforms into mullite at only above 1440°C . An exothermic effect, similar to that of kyanite has been observed.

According to the phase diagram only one compound, i.e. mullite, can be stable at ordinary pressure; all the other compounds are metastable and ultimately transform into mullite. All the transformations are monotropic, at every temperature mullite being more stable than the others, the metastable phases however may remain in this state for an unlimited time if the temperature does not reach the characteristic transformation temperature. The transformation temperatures may fall within the two characteristic temperatures, 1545°C - eutectic and 1810°C - melting point of mullite.

The more important factors that may affect the transformation are (1) the heating rate and (2) time of heating. The heating circumstances in Greig's investigations resulted in a characteristic sequence of transformations. Crystals of andalusite and kyanite transform initially at the edges, the transformation latter proceeding towards the centre. Sillimanite, however transforms in a bulk.

The study of transformation from a crystallographic point of view²⁹ confirms the sequence of transformation of the three minerals, though the temperatures of

transformation differ from these of Greig's results. The gradual transformation of andalusite and kyanite from pure homogeneous crystals to an aggregate of mullite and a vitreous phase is again observed. The colour of the products are quite different in that the vitreous phase formed from kyanite is greenish while that from andalusite is colorless. Moreover, the thermal mullitization of kyanite undergoes with such a considerable volume change that a characteristic crumbling occurs. In the case of andalusite the volume change is not so extensive.

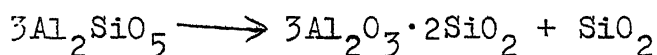
A qualitative investigation of the crystallization of the three anhydrous aluminosilicates, with due regard to the effect of pressure was done by Miyorhiro³⁰. The results indicate that mullite is the only stable mineral at ordinary pressures, while the other aluminosilicates become stable at higher pressures.

Keyser³¹ based on his electron microscopic and X-ray investigations into the transformations of kaolin, kyanite and sillimanite states that mullite is the final compound at equilibrium, at ordinary pressures, of all mixes or minerals of the system $\text{Al}_2\text{O}_3 - \text{SiO}_2$. However, he found, that these transformation processes have been influenced by even traces of contaminating substances.

The alkalis especially influence the transformation. The second usual phase is a glassy phase, in which the cristobalite formed during the transformation usually gets dissolved. The amount of cristobalite formed during transformation according to Keyser is inversely proportional to the amount of fluxes and to the amount of vitreous phases produced thereby. High glass content, which dissolves the silica formed, enhances the crystallization of mullite.

The study³² of the kinetics and of transformation of the sillimanite group minerals reveals that the reaction is essentially of first order. There has not been definite conclusions regarding the mechanism, however, kyanite particles of about 5 microns size seem to sinter and transform in a diffusion controlled process. The transformations have been studied through X-ray investigations for kyanite and andalusite and in the case of sillimanite, because of the almost indistinguishable nature of it, specific gravity measurements have been employed. Impurity effect on the transformation have been studied by adding soluble salts equivalent to 0.5 percent of the respective oxides. MgO has been the most suitable increasing the amount of mullite by about three times even at 1250 - 1350°C. Iron and sodium oxides are less effective. Kyanite is the easiest to transform followed

by andalusite and sillimanite. There were little traces of mullite even after 24 hours heating at 1450°C in the case of sillimanite. The activation energies proposed are 100 Kcal/mole for kyanite 140 and 170 Kcal/mole for andalusite and sillimanite respectively. All these materials, as reported earlier, transform following the equation,



It is also observed that the particle size plays an important role in the transformation, the finer the particles the more enhanced is the transformation.

1.4.2 FORMATION FROM KAOLIN TYPE MATERIALS

The transformation of kaolinite and other related materials is perhaps the most important series of reactions in the ceramic technology. Way back from 1887 innumerable number of investigations have been done to study the transformation, but still there is a lack of reliability and unambiguity regarding the theoretical explanations about the thermal effects on kaolin. The main difficult region for study is between 500 and 950°C when kaolin becomes amorphous for X-rays making this most reliable solid state investigation technique unreliable.

Some well defined reactions take place when kaolin or kaolin-bearing substances are heated. These have been proved using differential thermal analysis techniques. The characteristics of the enthalpy change versus temperature curve (DTA curve) of kaolinite, halloysite or any kaolinite type clay minerals in general are the following.

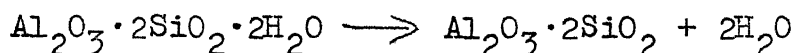
1. An endothermic (heat absorbing reaction) occurs between 500 and 600°C due to the release of hydroxyl ions. This is often referred to as the 'Water Loss' or 'Dehydration' which is rather a misnomer since kaolinite lattice has only 'OH' groups and not water.

2. A sharp exothermic reaction takes place between 900° and 1000°C more often known as the 'First exothermic effect'.

3. Kaolinite bearing clays show another exothermic effect between 1200° and 1300°C ('Second exothermic effect').

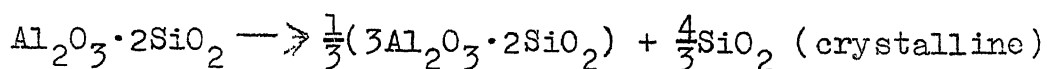
4. Some clays show another exothermic effect above 1300°C ('Third exothermic effect').

The endothermic effect is accompanied by the formation of metakaolinite with the dehydroxylation, occurring between 500 - 600°C. The reaction is



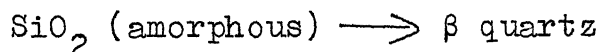
The first exothermic effect is perhaps the most widely disputed. There exist two schools of thought, one favouring the formation of mullite phase along with silica and the other the formation of a spinel along with silica. Roy³³ et al detected spinel phase at 850°C in their electron-diffraction work. Comer³⁴ also identified both spinel and mullite phase at 850°C in a kaolinite flake but at 950°C spinel disappeared and mullite was strongly in existence.

The work of Schieltz and Soliman³⁵ is of special significance with respect to the thermodynamic considerations of the kaolinite transformation. The free energy calculation from the enthalpy-entropy values of a series of reactions reveal that the most favourable reaction is,



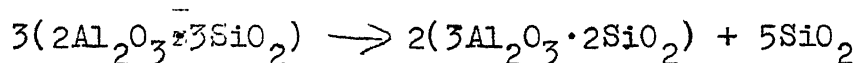
Considering the enthalpy changes in the possible reactions and the energy of crystallization of the various phases in question, the energy of crystallization of mullite was found out to be -336 Kcal/mole, the spinel -36.5 Kcal/mole and the quartz from the discarded amorphous silica -7.0 Kcal/mole. The contribution of mullite crystallization to the exotherm was derived to be -112 Kcal and that of the silica crystallization as -9.6 Kcal. The silica crystallization has been confirmed later by Nicholson³⁶.

The reaction proposed is



and the exothermic heat of reaction is -9 Kcal/mole whereas the heats of reaction when $4/3 \text{ SiO}_2$ or $1/2 \text{ SiO}_2$ crystallize at 980°C would be -12 Kcal/mole or -4.5 Kcal/mole respectively. Hence it is now observed that the first exothermic reaction is due to the formation of β -quartz crystals from amorphous silica discarded when the kaolinite transforms into mullite.

The second exothermic reaction between 1050 and 1100°C is thought by Brindley and Nakahira³⁷ to be the transformation of the spinel phase to mullite with further solution of silica. Further reactions end up in the formation of more of mullite of composition $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ and cristobalite. The combined reactions are given as



They have supported the theory of spinel formation with the discard of amorphous ^{silica} during the first exothermic reaction occurring between 950° and 1000°C .

There has been lot of contributions to both the schools of thoughts regarding the exact nature of phases present during the first and second exothermic

peaks. However it is more accepted that the formation of mullite type phase along with amorphous silica which later transforms to crystalline silica and the further crystallization of mullite are the causes of the respective exotherms and the transformation of the amorphous silica into cristobalite above 1300°C is the reason for the third exothermic peak around $1300 - 1400^{\circ}\text{C}$.

1.4.3 FORMATION FROM SYNTHETIC RAW MATERIALS

The formation of mullite from synthetic materials has been examined since as early as 1923 basically to copy the thermal effects of kaolin. Artificial mixes of alumina and silica in various proportions, mixes of synthetic materials which yield alumina and silica on heating have been used to study the formation of mullite and there has been a general success in all attempts, though the results obtained have been contradictory.

It is obvious that none of these artificial mixes, though made with a great care to bring about perfect homogeneity is identical with kaolin or its first products. The artificial mixes lack the layer arrangement of atoms as in kaolinite and metakaolinite. These may be said to have more or less a coarse linear series of particles in the three directions of space. Hence even though the transformation is construed to be the same as that of

kaolinite the heats of reaction shall be more in the case of artificial mixes.

A number of experiments have been made to determine the most favorable alumina/silica ratio for the mullite synthesis. The results have been quite contradictory and naturally so considering the fact that the formation depends on the processing technique whether it is sintering or fusion. Earlier³⁸⁻⁴¹ $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratios of 1:1, 2:1 and 3:2 were described as most favourable. Neuhaus⁴² explained the differences by the fact that sintering and fusion do not result in the same product, though the starting material is the same. Accordingly a $(3\text{Al}_2\text{O}_3 + 2\text{SiO}_2)$ composition yields $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ mullite if sintered and a composition $2\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ if fused. The melting point of the latter is 100° higher than that of mullite and differs from mullite in its 'a' and 'b' cell dimensions. An equimolecular mixture of alumina and silica also yielded the same products under the respective conditions.

The formation of single crystals of mullite is indeed difficult because under ordinary circumstances i.e. when silica volatilization is not prevented mullite melts incongruently. It was Bauer et al⁶ who first produced single crystals of mullite using Nerneuil technique and an oxyhydrogen flame and maintaining a

steep temperature gradient thereby circumventing the incongruent melting region and preventing the formation of corundum. The starting materials were calcined materials from repeatedly precipitated ammonium alum and silicic acid. This was followed by Barta and Barta¹³ who synthesized from varying mixtures of minerals have characterized a compound $5\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$ and identified as an individual mineral named Praguite. Under strong reducing conditions only corundum has been observed due to the volatilization of silica due to the increased H_2 content. Later Neuhaus and Richartz¹⁴ succeeded in synthesizing mullite single crystals varying from $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ to $2\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ depending upon the Vernicuil mount cooling.

The formation of polycrystalline mullite from materials apart from clays and gels has been attempted since the last few years. Several diverse techniques like cold pressing and sintering, hot pressing melting and quenching have been used. The formation of mullite from mixtures of α -quartz, silicic acid or β -cristobalite with diaspore (HAlO_2), gibbsite [$\text{Al}(\text{OH})_3$] or α -alumina has been studied by Wahl et al⁴³. Each of the silica containing materials was mixed with each of the aluminous materials in the ratio of 1:4, 2:3, 3:2 and 4:1 and fired to 1450°C . X-ray diffraction studies reveal that mullitization is influenced more by the structure of the starting materials

than by the mole percent variations. Diaspore combined with the forms of the silica to form mullite at lower temperatures than did gibbsite or corundum.

Preparation of mullite⁴⁴ from pure alumina and pure quartz resulted in some unreacted alumina and silica even though the mixing was intimate and the firing was done at 1500° - 1540°C for 12 days. Further confirmation of the results of Neuhaus and Richartz¹⁴ has been obtained from Fenstermacher and Hummel⁴⁵. They have attempted to sinter 3:2 and 2:1 compositions at 1710°C and 1650°C respectively, using 1% MgO to facilitate the reaction. Unreacted corundum has been observed in both cases, though considerably more in the 2:1 composition. The authors found that a mechanical mixture of 3:2 composition and α -alumina produced the identical X-ray patterns to fired 2:1 specimen. All the well authenticated examples of 2:1 mullite have been produced from melts. Thus it is concluded that 2:1 mullite is only metastable transforming into 3:2 composition on heating. The reason for this according to Aramaki and Roy¹⁹ is the formation of more four coordinated Al^{3+} ions in the liquid which do not rearrange to six coordination on cooling.

The method of formation of mullite certainly affects its morphology. It has been observed⁴⁶ that in

the absence of a liquid phase, mullite formed from the mixture of oxides resulted in chunky crystals, while the needle-like morphology invariably requires the presence of a liquid phase. It appears that mixing on a scale approaching to molecular levels is essential as in (1) reactive sputtering of oxides to form thin mullite films (Williams et al)⁴⁷, (2) thermal decomposition of kaolinite or (3) solidification from the melt to obtain mullite needles. Mullite made by melting and cooling is of 2:1 composition having a needle-shaped morphology, irrespective of the starting composition. However, on heating, this transforms to mullite of 3:2 composition and α -alumina retaining the acicularity.

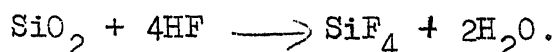
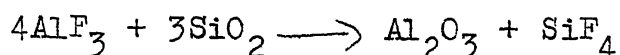
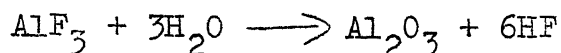
The growth of needles occur along the C-axis. Aluminium which is nearly always octahedrally coordinated in the crystalline state, can replace silicon and thus attain four-fold coordination at high temperatures, especially in glasses. Hence at the time of crystallization of mullite from the melt Al ions have equal ease to get to either four-fold or octahedral coordination. For the 2:1 composition, 2.8 tetrahedral Al must be added for every 2 octahedral Al to add another unit cell, while in the 3:2 mullite it is 2.5 for every 2 octahedral aluminium.

The process of sintering does not take place

during mullite formation and it happens only after mullite is formed. This has been observed by Budnikov et al⁴⁸ and Kroll and Polybayorinov⁴⁹. This is thought to be due to the arrest of sintering in the high temperature region due to the expansion and formation of a mullite 'framework'. It is a known fact that the formation of compounds in the binary and polynary silicate systems is often accompanied by a decrease in density within a certain temperature interval. The same has been true of mullite in the temperature region 1550 - 1650°C. An extension of the mullitization mechanism of the dehydrated kaolinite to that of mullite formation from the oxides shows that silica diffuses into porous grains of alumina, creating pores in places where silica had been and the expansion of the samples due to mullite formation. The fact that the surface energy of the system due to the fine grinding of starting materials is used up on mullite formation and the construction of mullite lattice and the excess energy obtained during the chemical reaction is lost in the spontaneous correction of lattice defects has been logically and practically explained by Kroll and Poluboyarinov⁴⁹, by sintering mixtures of mullite obtained from the oxides at three different temperatures; the beginning and end of mullitization and the beginning of sintering. This has resulted in a completely dense

material at nearly 1700°C caused primarily by the fine milling and the higher reactivity of the incompletely sintered mullite.

The formation of mullite from AlF_3 and kaolin and $\text{AlF}_3 + \text{SiO}_2$ has been extensively studied by Locsei⁵⁰. The formation of mullite from AlF_3 (97.9% $\text{AlF}_3 + 1.9\% \text{Al}_2\text{O}_3$) and Zettlitz kaolin (Al_2O_3 38.5, SiO_2 46.95, other oxides 2.0, heat loss 12.8) in the ratio of 39.5 to 60.5 occurred at 1100°C. The possible reactions occurring are proposed to be



Stoichiometric $2\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ was formed when the mixture was heated. The heating allowed equilibrium to occur at 550° - 600°, 700° - 750° and 800 - 950°C. The final products seem to depend on the heating rate and ratio of fluorine leaving as SiF_4 . At the optimum heating rate if the above ratio is 0.47 the product is mullite and at > 0.5 and < 0.42 corundum and mullite + silica phases develop. The activation energies of mullite formation and kaolin dehydration have been reported to be 960 and 99.8 cal/gm respectively.

The formation of mullite from AlF_3 and SiO_2 is believed to be the last stage of a two step reaction. The first stage consists of the formation of topaz, accompanied by the emission of SiF_4 at $700 - 900^\circ\text{C}$ and 600°C respectively. The evolution of SiF_4 continues during the second stage at 900°C simultaneously with the formation of mullite. The final product depends on the $\text{AlF}_3 : \text{SiO}_2$ ratio; with it at < 1.29 the products are quartz and mullite; at 1.29 $<$ ratio < 1.87 - the products are mullite and corundum and at > 1.87 the product is corundum. Water acts as a catalyst reacting with AlF_3 to form HF which in turn reacts with silica to form SiF_4 .

The synthesis of mullite from various synthetic raw materials yielding the respective oxides on heat still, continues to be an active field of study and there have been lot of patents on the various methods of synthesis. The more common materials used are Diaspore, clays, gibbsite, bayerite AlF_3 as the alumina yielding sources and quartz, cristobalite flint and other silicious compounds. Most of these studies are done to synthesize mullite in situ in the ceramic bodies. However considerable studies are also on for making sintered mullite as a raw material for further applications.

1.4.4 FORMATION FROM GELS

It has been known long since that it is gels and not the artificial mixes that give a suitable, finely dispersed material of high reactivity, as a starting material. The earliest attempts to form mullite from coprecipitated gels of alumina and silica were to study the thermal characteristics of gels. Coprecipitated gels made from sodium silicate and aluminium chloride⁵¹, from aluminium nitrate with ammonium hydroxide sodium metasilicate with an excess of HCl⁵² reacted to form mullite over 1100°C. In samples with higher silica and alumina content cristobalite and corundum were the other phases present. The mullite formed in the latter case was of $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ composition, at least this ratio gave the highest yield of mullite. The non-observance of solid solutions contradict the recent authoritative phase equilibria studies.

Gels prepared from alkali silicates are nearly impossible to purify. Several methods have thus been proposed to eliminate these difficulties. Coprecipitation⁵³ from ethyl orthosilicate and aluminium sulfate solution by ammonium hydroxide yielded gels of the ratio $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ which when heated above 950° have shown the presence of mullite only. Roy⁵⁴ has improved upon this

through the precipitation of silica by the addition of HCl to ethyl orthosilicate. Previously added aluminium nitrate is adsorbed on the surface of the gel. Evaporation of the water and ethyl alcohol obtained during hydrolysis result in a highly reactive gel which when fired at 450°C yield amorphous highly reactive oxides.

Bidel and Jouenne⁵⁵ formed mullite at 960° with an exothermic reaction between amorphous alumina and silica gels in a water suspension. A second exotherm at 1215°C occurred as a result of the formation of secondary mullite from silica and alumina.

Otani and Kojima⁵⁶ thermally decomposed methyl-siloxy aluminium compounds to prepare gels with $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratios of 1.61, 1.38, 1.04, 0.612 and 0.141. A 'mullite-like' phase was detected above 1050°C in the last composition and at above 900°C in the rest. However mullite as a distinct crystalline phase was detected only above 1400°C in all but the first mixture.

Crofts and Marshall⁵⁷ have suggested another unique method of forming mullite. The technique essentially consists of a slow injection of 10 percent solution of AlCl_3 and SiCl_4 in the appropriate Si/Al ratio in the diethyl ether layer through a rubber diaphragm into a rapidly stirred solution of approximately 6 volume percent

ammonia maintained at 50°C . An amorphous colloidal precipitate thus formed reacts at 1400°C to yield mullite as the only phase.

A more convenient, easier and cheaper method of synthesis of high purity mullite has recently been reported by Ghate et al⁵⁸. The method involves gelation of γ -alumina and amorphous silica at a pH of 6 - 7, drying the gel at the rate of 120°C , followed by crushing and screening through 120 mesh. The powder thus obtained is heated at 1400°C for 20 hrs. The resulting powders are of 1 μm in size and have less than 100 ppm impurities. Particle morphology is rather globular and mullite is the only phase present.

The formation of mullite from gels have been investigated from all angles, academic through industrial applications. Even though the temperature of mullite formation is considerably reduced due to the higher reactivity of the starting materials, the cost of the pure raw materials and processing make the product too costly for a large scale production. However for a ultra pure mullite for specialised applications, the formation from gels is a more prospective way.

1.5 EFFECT OF MINERALIZERS ON MULLITE FORMATION

There have always been efforts to form mullite from the various materials concerned at a lower temperature of firing or to have a higher yield. The use of admixtures for this purpose or mineralizers have been thought of and studied in detail quite extensively. It is generally agreed that the mineralizers influence the quality and/or the quantity of the products. These foreign substances also influence the quantitative phase distribution. Several authors claim to have succeeded in increasing the mullite content of some ceramic wares by judicious use of certain mineralizers. However, the results are extremely contradictory, even to the extent of diametrically opposed effects on the same material with the same mineralizers. Moreover there is no fully reliable theory put forward to explain the effect of mineralizers on the formation of mullite.

The effect of mineralizers on the formation of mullite had been noticed as early as 1928 by McVary and Hursh in refractory bricks of diaspore which get enriched in alkali oxide and vanadium pentoxide on their surfaces. Magnetite according to them is a good mineralizer. Since then there has been lot of work done to study the

effect. The studies include apart from a large list of mineralizers, variation in temperatures, firing time, starting materials, amount of mineralizers and firing conditions. Every individual author has produced his own results and optimum conditions. Observations have also been made regarding failure of the same mineralizers under conditions like (i) exceeding the optimum percentage (ii) above an optimum temperature and time of firing and (iii) in the case certain starting materials. The detailed investigations of the various authors are produced in a tabular form (see Table I.2).

It was Budnikov⁶⁴ who first tried to set things right in this chaotic problem of mineralizers. Their most important achievement is to have noticed that the effect is a function of the ionic radius to ionic charge ratio (r/e) i.e. the order of effectiveness decreases as the r/e ratio decreases. But this has been contradicted by Mazarenko and Sviridenko (1954) whose hypothesis is diametrically opposite. Their contention is that in the case of an identical charge the mineralizing effect grows proportionately to the decrement of the ionic radius.

The other theory explaining the effect of mineralizers is the formation of a molten phase which accelerates mullite formation and crystallization.

Table 1.2: Studies on the Effect of Mineralizers

Author	Ref. No.	Experimental Details	Results and Discussion
Yoshioka and Isomachu (1930)	59	Admixtures: Fe_2O_3 , B_2O_3 , Steatite, Orthoclase Talc, CaO , CaF_2 Temp. of firing: 1400°C , Time = 1 hr Mullite determination by HF residue	Sequence of efficiency Fe_2O_3 , B_2O_3 , Steatite Orthoclase, talc, CaO and CaF_2
Kraner (1938)	60	Fusion of α -quartz and $\alpha\text{-Al}_2\text{O}_3$ Additions: Na_2CO_3 (4.5%), Li_2O (2%) and CaO (>10%) cast as refractories	Mullite formation, prevented by these additions. Only crystalline constituent was corundum
Nakai and Fukami (1939)	61	Starting materials: Korean kaolin, Kaolin-alumina mix and a quartz-alumina mix Mineralizers - $\frac{1}{2}$, 2 and 5 Firing temperatures - 900 to 1450°C mostly oxides, tungstates and molybdates were studied	Every substance has its temperature interval of optimum effect 900 - 1000°C - Molybdenum and Boron compounds are effective General use - Copper is useful For high temp. - Manganese (> 1300°C)

Continued...

Table 1.2 continued.

Parmelee; Rodrigues (1942)	62	Mineralizers: Oxides of Zn, Li, Mg, Fe, Mn, Ce, Mo, Na, K, Ti, Sn, B and Ca. Temp. of firing - 1300, 1400 and 1500°C HF leaching for the quantitative determination	Oxides of Zn, Li, Mg, Fe, Ce and Mo - good mineralizers Boric oxide and CaO - fair Na, K, Ti and Sn oxides - Bad proportion of mullite appreciably affected by 1% mineralizers. Larger variation had little effect Li ₂ O, MgO and ZnO were especially good at temperature $\approx 1400^{\circ}\text{C}$
Akiyama and Kadogawa (1943)	63	Mineralizers: AlF ₃ , AlCl ₃ , Al ₂ (SO ₄) ₃ , NaCl, Na ₂ CO ₃ and HCl Parameters: Quantity 1-5 percent; Firing time - 2 hrs; Firing temperature: 1430°C Method of phase composition control - X-ray and microscope	The most effective ones are Na ₂ CO ₃ and in a lower degree Al ₂ (SO ₄) ₃
Budnikov and Shmukler (1946)	64	Clays and kaolins subjected to a firing of 1000 - 1600°C. Time periods - 1, 3 and 18 hrs.	Larger the value of the ratio of ionic radius to the ionic charge, more effective is the mineralizer

Continued...

Table 1.2 continued.

Palmeri (1951)	65	Kaolinite fired between 945 and 1350°C with and without admixtures. Percentage of admixture was constant - 3 percent. Optical, electron-optical and X-ray methods for mullite detection	First mullite reflections of the HF residue was observed just above 945°C if the firing lasted for 30 hours. Sequence of effectivity of mineralizers used: CaF_2 , B_2O_3 , CaO , LiCl , MnO_2 and finally MgO .
Skinner et al (1953)	66	Mineralizing effect of TiO_2 , Fe_2O_3 and of alkali oxides	Mineralizing effect of TiO_2 depends greatly on $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio. In certain cases adding 5 TiO_2 is more effective than 10% Al_2O_3 . Fe_2O_3 is good when added less than 5%. Alkali oxides have no positive effect. They even decrease mullitization
Avugustinik et al (1954)	67	Mullite formed from 3 parts Al_2O_3 and 2 parts SiO_2 in the presence of Li^+ , Na^+ , K^+ , Mg^{2+} , Zn^{2+} , Ca^{2+} , Ba^{2+} , Cr^{3+} , Fe^{3+} , Ti^{4+} and Mn^{4+} at 1400°C for 4 hrs	For the same valence, the effectiveness increased as the radius of the cation decreased, and for the same radius it was greater for lower valence cations

Continued...

Table 1.2 continued.

Moore and Prasad (1955)	68	'Kaolin-alumin mixtures,' All except ferric oxide corresponding to silli- manite and mullite compositions were fired in the temp. range of 1300-1600° for 24 hrs. The quantity of product was determined by X-ray. Mineralizers: Salts of Na, K, Li, Mg and Ca and oxides of Mn, Ti and Fe	gave maximum amount of mullite when added in quantities of 1 percent or less. Additions more than than 'optimum' amount decrease mullite formation to even less than that without any mineralizers 'Break down' of the mullite phase occurs in these cases forming glass and conrundum rich phases
Nazarenko and Sviridenko (1956)	69	Experiments on mixtures of β -quartz and γ -alumina heated to 1000-1600°C. Additions: Fluorides, chlorides and carbonates of Li, Na, K, Mg and Ca. Oxides of Zn, B, Cr, Fe, Mn and Ti.	Degree of mullitization increased with the decrease of cation radius, Li^+ and B^{3+} ions were the most effective, with the smallest cation radii. There appears to be an optimum temperature of heating and an optimum duration of heating for each mineralizer.

Continued...

Table 1.2 continued.

Budnikov et al (1963)	70 '3:2 coprecipitated gels of SiO_2 and Al_2O_3 with Ba^{2+} , Ca^{2+} , Be^{2+} , B^{3+} , Ti^{4+} , Mn^{4+} , Mg^{2+} , Fe^{3+} and Ni^{3+} as mineralizers, fired at 1350°C .	'Degree of mullitization without admixtures = 53 with Ba^{2+} , Ca^{2+} and Be^{2+} = 91, 88 and 75 respecti- vely. The ions B^{3+} , Ti^{4+} , Zr^{4+} , Mn^{4+} and Mg^{2+} were ineff- ective. Fe^{3+} and Ni^{3+} decreased mullitization by 46% and 40% respectively. Conclusion: yield is directly proportional to the radius/charge ratio of the cations
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Chaudhri (1969)	71 Influence of alkalis, alkaline earth oxides, Fe_2O_3 and TiO_2 on mul- litization in kaolin - studied using X-ray diffraction techni- ques.	Na_2O , K_2O and CaO were most effective at lower concentrations (1%) - whereas TiO_2 and Fe_2O_3 enhanced mullitization when added in amounts of approximately 4%.
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right. The presence of volatiles, have also been observed to have a positive effect.^{72,73} It has also been observed that certain admixtures decrease the quantity of mullite produced.

Grofczik, however, is of the firm conclusion that the contradictions are due to the methodological errors in detecting and determining the mullite content by X-ray, planimentering and dissolution by hydrogen fluoride. Based on their investigations⁷⁴, they conclude that the quantity of mullite is never increased by the presence of mineralizers, or the heating temperature or time. The maximum stoichiometric quantity of mullite is always obtained provided the temperature and time of firing is sufficient for the solid-state transformation. However, there is a well pronounced effect on the mullite crystals - their size and specific surface get altered by the presence of admixtures. The size increases even by two orders of magnitude accompanied by a drastic reduction in the specific surface.

A more recent investigation by McKenzie⁷⁵ provides a lot of information about the various mineralizer effect. He has examined the effect of 28 exchangeable cations and 21 exchangeable anions as well as the effect of atmosphere on mullite formation. The summary of their

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conclusions is as follows:

- (1) Alkali and alkaline earth cations effect the formation proportional to their size to charge ratio.
- (2) The transition metal cations act according to their oxygen affinity.
- (3) The kinetic studies on the transformation of homo-ionic clays reveal that the mechanism involves a nucleation controlled rate step. The cations are ~~thought~~ to influence the rate of formation of mullite by providing lattice sites of suitable energy for nucleation.
- (4) In the case of anions, their inclusion in the lattice due to their size effects and the repression of formation by tetrahedral ion is thought to involve the modification of the reactivity of the silica network by surface adsorption effects. When an anion forms stable complexes with the cations in clays the reduction in mobility adversely affects the formation of mullite, while the least stable anions containing nonmetallic atoms, inhibit the formation the least, suggesting dissociation at high pressures.
- (5) The transformation of clay is greatly enhanced by water vapor, and vacuum.

Nitrogen and hydrogen have a less pronounced effect while oxygen and CO_2 retard the formation.

The complexity of the results with all their contradictions provide lot of difficulties for one to make a choice of a mineralizer to enhance mullitization. However, considering the starting materials, temperature and time of firing, atmosphere etc., the choice is to be done for a successful product. However, some of the accepted positive mineralizers are iron oxide, magnesium carbonate, zinc oxide, calcium oxide, boric oxide, tin oxide, copper oxide, manganese oxide and fluorides like AlF_3 , CaF_2 , BaF_2 , Na_2SiF_6 etc.

1.6 PROPERTIES AND APPLICATIONS

Mullite is a characteristic constituent of all ceramic products made from aluminosilicates. Mullite ceramics are technologically attractive because of their excellent high temperature mechanical stability and thermal shock resistance. The various properties - structural, thermal, mechanical, chemical, and **electrical** are given in the tabular forms (see Tables 1.3 to 1.7).

The applications of mullite constitute a wide spectrum from huge fusion cast refractories to small

Table 1.3: Structural Properties of Mullite

Property	Value								
Formula wt (g/mole)	425.94								
Crystal system orthorhombic ($^{\circ}\text{\AA}$) - a	$7.584 \pm .003$								
b	$7.693 \pm .003$								
c	$2.890 \pm .001$								
Unit cell volume ($^{\circ}\text{\AA}^3$)	168.61 ± 20								
Theoretical density (g/cm^3)	$3.16 - 3.22$								
Melting point ($^{\circ}\text{C}$)	1850								
Hardness (Mohs)	7.5								
Index of refraction (n_D)	1.65								
Birefringence	0.012								
Optical character	positive								
Crystal habit	Acicular or Prismatic								
Positions and intensities of three strongest X-ray diffraction	<table> <tr> <td>hkl</td><td>$d, \text{\AA}$</td></tr> <tr> <td>120</td><td>3.42</td></tr> <tr> <td>121</td><td>2.21</td></tr> <tr> <td>331</td><td>1.53</td></tr> </table>	hkl	$d, \text{\AA}$	120	3.42	121	2.21	331	1.53
hkl	$d, \text{\AA}$								
120	3.42								
121	2.21								
331	1.53								

Table 1.4: Thermal Properties of Mullite

Property	Value
Conductivity, κ , porosity [Cal/sec/cm ² /°C/cm]	
100°C	0.0145
200°C	0.0132
400°C	0.0113
600°C	0.0103
800°C	0.0097
1,000°C	0.0095
1,200°C	0.0093
Expansion ($\times 10^{-6}/^{\circ}\text{C}$)	
at 20 - 1325°C	4.5
25 - 500°C	4.63
25 - 1000°C	5.13
25 - 1500°C	5.62

Table 1.5: Mechanical Properties of Mullite

Property	Value
Shear strength at 1100°C ($\times 10^3$ psi)	2.4
Young's modulus density = 2.77 g/cm ³ ($\times 10^6$ psi)	
at 25°C	18.4
400°C	18.9
800°C	14.8
1200°C	4.0
Modulus of rigidity nonporous ($\times 10^6$ psi)	
at 25°C	8.5
500°C	7.1
900°C	4.8
1000°C	4.2
1100°C	4.0
Shear modulus $d = 2.779$ gm/cm ³ at r.t ($\times 10^6$ psi)	8.38
Bulk modulus ($\times 10^6$ psi)	13.20
Modulus of rupture $d = 2.77$ ($\times 10^3$ psi)	25 - 8500 400 - 13500 800 - 16700 1200 - 11500
Poisson's ratio $d = 2.779$ (r.t)	0.238
Creep at 1200 psi; 1100°C ($\times 10^6$ in/hr)	0.4
Deformation under load (%)	
50 psi at 1450°C	0
25 psi at 1650°C	2

Table 1.6: Chemical Properties of Mullite

Property	Value
Chemical nature	Slightly acid
Limit of usefulness ($^{\circ}\text{C}$)	.
in air	1800 $^{\circ}$
in vacuum	1500 - 1700
Stability	
in reducing atm	Fair
in carbon	Fair
in acid slags	Good
in basic slags	Fair
in metals	Fair
in most acids	Insoluble

Table 1.7: Electrical Properties of Mullite

Property	Value
Dielectric constant	6
Specific electrical resistance	
ohm cm	
at 600°C	10^6
1400°C	10^4

crucible and ceramic ware and recently electronic substrates.

The high alumina refractories which constitute the most important and the most diversified groups refractory materials offer improved resistance to abrasion, spalling, impact or load, high refractoriness as well as excellent resistance to corrosion by acid slags at high temperatures. A good mullite refractory consists on an average 85 percent mullite by weight. The glass should not exceed 5 percent by weight and it should be highly siliceous and have a high viscosity. Unreacted alumina to the extent of 5-6 percent is also an usual occurrence.

The areas of application of mullite refractories include metallurgical industries where these are used as electric arc furnace roofs, hot metal mixers, heating furnaces, and low frequency induction furnaces. In glass industry mullite is used in the form of blocks in the upper structure of the glass tank and for constructing the drawing chambers of the furnace. Mullite is also used as kiln setting slabs, posts for firing wares and lining for high temperature reactors.

Fused mullite is the normal raw material for mullite refractories. However, the use of sintered mullite is also quite considerable. Sintered mullite

CHAPTER 2

STATEMENT OF THE PROBLEM

The objective of the present investigation is to make mullite by sintering at a lower temperature than that usually adopted. The product aimed at is to have as good properties as of conventional fused mullite and be as a low cost as that of sillimanite. Since the cost of the end product is an important factor, the raw materials and the processing techniques have to be appropriately chosen.

The study consists of two parts, (a) preparation of sintered mullite and (b) characterization of the product.

Preparation of Sintered Mullite:

The preparation of sintered mullite was studied with the following parameters.

(i) Raw materials:

A huge list of raw materials exist for the production of sintered mullite. The more important and widely used ones, however, include kaolins or china clays, diaspore, kyanite, gibbsite, bayerite, bauxite as the sources of alumina, clays, quartz flint, fused quartz and of late paddy husk ash as the sources of silica. There are many combinations of the above materials for making

sintered mullite.

The raw materials used in the present study are limited. They are Kundra (Kerala) china clay, alumina $A = 2$ and $A = 16$ and Hydral 710 - a hydrated alumina - all from The Aluminium Company of America (ALCOA), Bayer Alumina from Madras Aluminium Company Ltd. (MALCO) and Flint Dust Collector fines.

(ii) Alumina/Silica ratio:

The alumina/silica ratio was varied slightly around the theoretical mullite composition $72 \text{ Al}_2\text{O}_3/28\text{SiO}_2$, by varying the amounts of clay and alumina in the starting mix composition. The mix compositions were of the clay to alumina ratios as 45/55, 50/50, 53/47, 55/45 and 57/43. These ratios correspond to the $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratios 76.70/23.30, 73.9/26.1, 72/28, 71.1/28.9 and 72/28 ($\approx 10\% \text{ SiO}_2$ evaporation) respectively.

(iii) Sintering temperature:

The sintering temperatures were 1400°C , 1450°C , 1500°C , 1550°C and 1600°C . The 1400°C runs were taken in Globar resistance furnaces and the others in oil fired (1450°C) and gas fired furnaces.

(iv) Soaking time:

The soaking times at the various peak temperatures

sintered mullite.

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(iii) Sintering temperature:

The sintering temperatures were 1400°C , 1450°C , 1500°C , 1550°C and 1600°C . The 1400°C runs were taken in Globar resistance furnaces and the others in oil fired (1450°C) and gas fired furnaces.

(iv) Soaking time:

The soaking times at the various peak temperatures

were 6 and 12 hrs at 1400°C; 6 hrs at 1450°C; 3 hours at 1500°C and 2 hours at 1600°C.

(v) Mineralizers:

The effect of mineralizers was indeed an important parameter in the study. A whole range of mineralizers have been tried and their effects on mullitization have been studied. The mineralizers include oxides of zinc, magnesium (as carbonate), copper, manganese, boron, titanium, fluorides of calcium and aluminium and cryolite and sulfates of copper and manganese. These inclusions have to be kept at a minimum so that the ultimate product can be pure having less glassy phase. It is important that the glassy phase in the product is kept at a minimum since it affects the high temperature properties. Free alumina as corundum is tolerable since it does not seriously affect the high temperature properties. In fact it provides better strength at high temperatures.

Characterization of the Product:

The characterization was done by studying the following properties (i) density, (ii) porosity, (iii) shrinkage, and (iv) modulus of rupture.

Phase analysis was done primarily by X-ray diffraction studies and later confirmed by chemical analysis and photomicrography. Quantitative determination of the

mullite in the product was also carried out in certain products.

The intended applications of the product are (i) as a refractory raw material for the manufacture of high alumina and mullite super refractories, (ii) as a grog in the super refractory castables and (iii) in ceramic wares for high temperature applications like crucibles, furnace tubes thermocouple sheaths etc. where the product (sintered mullite) is formed in situ.

CHAPTER 3

EXPERIMENTAL

3.1 PREPARATION OF MULLITE

3.1.1 RAW MATERIALS

There exists a wide range of raw materials from which mullite can be synthesized. The choice of the raw materials was governed by the following factors (i) Cost of the raw material (ii) Quality and availability (iii) Ease of formation of mullite from these materials and (iv) Reliability of the source of the materials with regard to the quality of conformance and consistency of the supplies.

The final choice includes uncalcined china clay from Kerala as the major source of alumina and silica and for the extra alumina needed for the complete transformation, various types of aluminas $\Lambda = 2$, $\Lambda = 16$ and the hydrated alumina, hydral 710 from ALCOA and Bayer alumina from MALCO were used. The ALCOA aluminas have been used since they are the industrial standards for the production of sintered alumina and mullite all over the world. However, the MALCO alumina seems to be a good replacement and hence it has also been used.

The various types of alumina were used to exploit some of their different characteristics for the mullite synthesis. $\Lambda = 2$ alumina is a coarser calcined alumina but quite cheaper compared to $\Lambda = 16$ and hydral 710. $\Lambda = 16$ alumina is a very fine, superground powder of median particle size of about 0.5 micron and is highly reactive. It sintered to 99 theoretical density when fired to 1550° for 1 hour. The hydral 710 is actually $\text{Al}(\text{OH})_3$ - a hydrated alumina with about 35% water. On calcining, it forms $\gamma\text{-Al}_2\text{O}_3$ which is also very reactive. MALCO alumina even though coarsest of the lot is cheapest and above all is an indigenous material. It has proved to be a good replacement for $\Lambda = 2$ in other applications.

Some typical properties of the various starting materials are presented in Table 3.1.

The mineralizers used were fine powders (minus 325 ~~#~~ A.S.T.M.) and of Lab reagent quality. These were added in specified amounts per 100 gms of each mix. The amount of mineralizers added was kept within a certain range the maximum amount being 1 to 5% depending on the mineralizer, to minimize glass formation.

3.1.2 PREPROCESSING OF RAW MATERIALS

The china clay from the attritor house (finer than about 50 microns) was sieved through A.S.T.M. 325

Property		Chila Clay	A = 2 alumina	A = 16 SG alumina	Malco alumina	Hydral 710 Alcoa
1. Chemical analysis						
Al ₂ O ₃ percent (wt)	36-40	99.2	99.5+	198.5 min	64.5 min
SiO ₂ percent (wt)	45-48	0.03	0.08	0.04 max	0.02 max
Fe ₂ O ₃	-do-	0.72 max	0.05	0.01	0.04 max	0.008 max
TiO ₂	-do-	2.0 max				
Na ₂ O/K ₂ O	-do-		0.60	0.08	0.80 max	0.35 max
MgO					
CaO					
Ignition loss	-do-	13-14	0.5	1.00 max		
2. Density gms/cc		2.5-2.7 (2.53)	3.8-3.9 (3.88)	3.8-3.9	3.7-3.9	0.352 (packed bulk density)
3. Fineness						
<u>Finer than</u>						
50 microns ... percent		74.87	67.27		+100 mesh	
40 microns ... percent		62.33	59.93		-10.00	1 micron
30 microns ... percent		2.87	58.73			median
20 microns ... percent		1.60	20.40		-325 mesh	
10 microns ... percent		1.33	10.33		-20 max	size.
5 microns ... percent		0.50	7.60			

mesh and the finer fractions were analysed for the particle size using the Andreason's pipette technique.

The A = 2 alumina was ground in a pot mill for 24 and 48 hours respectively using a charge to grinding media ratio of 1 to 4. The pot was made of high alumina porcelain and so were the grinding media. The particle size of the as received and the ground materials were also analysed by Andreason's pipette method. The analysis is presented in fig. 3.1.

The Dayer alumina from Malco (which is finer than 240 mesh A.S.T.M.) is ground in a ball mill for 12 hours with a charge to media ratio of 1 to 2 using a porcelain jar and 1" porcelain balls. The fine powder thus obtained was 95-99% finer than 325 mesh A.S.T.M.

3.1.3 MIXING AND MOULDING

MIXING

Based on the composition of china clay (37% Al_2O_3 and 48% SiO_2) and considering the formation of mullite of 72 alumina and 28 SiO_2 composition, mixes having varying amounts of clay and alumina were prepared. Initially clay to alumina ratios of 45/55, 50/50, 53/47 and 55/45 were tried to study the effect of the composition variation on the phases formed. Based on the X-ray

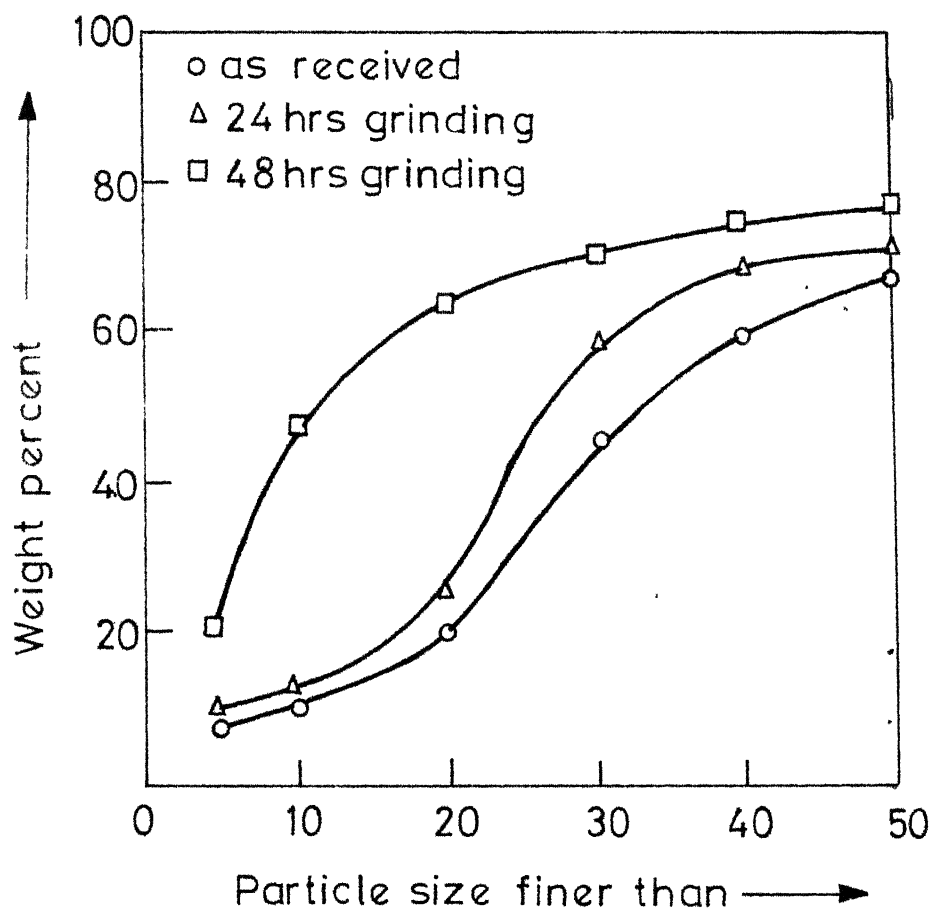


FIG. 3.1 EFFECT OF GRINDING ON PARTICLE SIZE OF ALUMINA (A=2 Alcoa)

results it was then concluded that the ratio 55/45 is the most suitable and a higher clay to alumina ratio of 57/43 was also tried assuming that about 5 percent of silica evaporates. Hence later, for more detailed studies the ratios were primarily 55/45 and 57/43. Apart from these, combinations of $A = 2$ and $A = 16$ and $A = 2$ and Hydral 710 with the same ultimate ratio of 55/45 were also tried to study the effect of these highly reactive aluminas on mullite formation. In both the cases part of the $A = 2$ alumina was replaced by the respective additions. In the case of Hydral 710 additions the ultimate alumina obtained from the Hydral 710 on heating was the basis (e.g.) for 10 gms of Al_2O_3 to be replaced, the amount of Hydral 710 ($65\% Al_2O_3$) was $10/0.65 = 15.38$ gms.

Tables 3.2, 3.3 and 3.4 give the details of the various mix compositions used.

The mixes were prepared by mixing in a pestle and mortar or in a plastic bowl, each time care being taken to achieve intimate mixing. About 5-8 percent by weight of water was added to wet the mix after about 10 minutes of dry mixing. Then further mixing was done, crushing the small balls formed due to coagulation, from time to time. There was no addition of a temporary binder or a lubricant since water itself was a good

Table 3.2: Nomenclature Details of Various Mixes

[Fired at 1400°C (Globar furnace for 6 hours)]

Nomenclature	Component (Weight Percent)			
	China clay	A = $2\text{Al}_2\text{O}_3$	Hydral 710	Mineralizer
1a	55	45		
1b	55	30	23.07	
1c	55	45 ^a	-	
1d	55	45 ^b	-	
2a	50	50	-	
2b	45	55	-	
2c	50	40	15.38	
2d	50	30	30.77	
2e	50	20	46.15	
2f	50	10	61.53	
3a	25		34.00	
3b	25		30.00	
Th	53		47.00	
C	55	45	-	Cryolite - 1.0
Cu	55	45	-	Copper oxide - 1.0
B_2O_3	55	45	-	Boric oxide - 1.0
Mg	55	45	-	Magnesium carbonate-2.0
Mn	55	45	-	Manganese oxide - 1.0
Zn	55	45	-	Zinc oxide - 1.0

a. ground for 24 hrs in a ball mill

b. ground for 48 hrs in a ball mill.

Table 3.3: Details of Mixes Fired at
1400°C for 12 hrs and at
1500°C for 3 hrs.

Nomenclature	Constituent (weight percent)				
	China clay	A = 2 alumina	A = 16 alumina	Hydral 710	Mineralizer
1A	55	45	-	-	-
1B	55	30	-	23.08	-
1BX	55	30	15	-	-
1E	55	35	-	15.38	-
1EX	55	35	10	-	-
1F	55	40	-	7.69	-
1FX	55	40	5	-	-
1G	50	39	-	-	-
2G	50	37	-	-	-
3A	25	-	-	39.00	-
3B	25	-	-	37.00	-
AFA	55	45	-	-	AlF ₃ - 1.0
AFB	55	45	-	-	AlF ₃ - 2.0
AFC	55	45	-	-	AlF ₃ - 5.0
B ₂ A	55	45	-	-	B ₂ O ₃ - 1.0
B ₂ B	55	45	-	-	B ₂ O ₃ - 2.0
B ₂ C	55	45	-	-	B ₂ O ₃ - 3.0
CA	55	45	-	-	Cryolite - 1.0
CB	55	45	-	-	Cryolite - 2.0

Continued...

Table 3.3 continued.

Nomenclature	Constituent (weight percent)				
	China clay	A = 2 alumina	A = 16 alumina	Hydral 710	Mineralizer
CAA	55	45	-	-	CaF_2 - 1.0
CAB	55	45	-	-	CaF_2 - 2.0
CAC	55	45	-	-	CaF_2 - 3.0
CAO	55	45	-	-	CaO - 1.0
CuA	55	45	-	-	CuO - 0.5
CuB	55	45	-	-	CuO - 1.0
CuC	55	45	-	-	CuO - 1.5
CuD	55	45	-	-	CuO - 2.0
CuE	55	45	-	-	CuO - 2.5
CuBX	55	45	-	-	CuO as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ soln. - 1.0
MgA	55	45	-	-	MgCO_3 - 1.045
MgB	55	45	-	-	MgCO_3 - 2.090
MnA	55	45	-	-	MnO_2 - 0.5
MnB	55	45	-	-	MnO_2 - 1.0
MnAX	55	45	-	-	MnO_2 as MnSO_4 soln. - 0.5
MnBX	55	45	-	-	-do- -1.0
FA	55	45	-	-	Fe_2O_3 - 1.0
K	55	45	-	-	Raw kyanite - 5
TiA	55	45	-	-	TiO_2 - 1.0
ZnA	55	45	-	-	ZnO - 0.5
ZnB	55	45	-	-	ZnO - 1.0

Table 3.4: Details of Mixes Fired at 1450°C Refractory
Kiln and 1600°C for 2 hrs.

Nomenclature	Constituents (weight percent)			
	China clay	$\Lambda = 2$ alumina	Malco alumina	Mineralizers
M1A	55	45	-	-
M2A	60	45	-	-
M1	55	-	45	-
M2	60	-	45	-
M1X	55	-	45 (Super ground)	-
M2X	60	-	45 (Super ground)	-
M1A1	55	45	-	MgCO ₃ 2.09
M2A1	50	45	-	MgCO ₃ 2.09
M1A2	55	45	-	ZnO 0.5
M2A2	60	45	-	ZnO 0.5
M11	55	-	45	MgCO ₃ 2.09
M21	60	-	45	MgCO ₃ 2.09
M12	55	-	45	ZnO 0.5
M22	60	-	45	ZnO 0.5
M1X1	55	-	45 (Super ground)	MgCO ₃ 2.09
M1X2	60	-	45 (Super ground)	ZnO 2.09
FM	(Flint) ^φ = 72	-	28	-
FA	(Flint) ^φ = 72	28	-	-

^φ Dust collector fines.

enough binder and the green samples were hard enough to handle even after drying.

MOULDING

After mixing, the pellets of about 1" in diameter and about 1/4 to 3/4" in thickness were made by pressing in steel die under a Laboratory hydraulic press. The typical pressure used was between 10000 to 15000 psi.

The pellets were then air dried in atmosphere and the green densities were measured from the diameter, thickness and weight data. The diameter and thickness were measured using a Vernier calipers (Least count = 0.02 mm). A good representative sample was taken in each case and the diameter and thickness were measured at 4 places in each sample and the average values were taken for calculations. Green density data are furnished in Table 3.5.

3.1.4 SINTERING

The pellets were then sintered at temperatures of 1400°C, in a globar furnace, 1450°C in an oil fired refractory kiln having a five day cycle, 1500°C and 1600°C in gas fired furnaces. The soaking time at the maximum temperatures were 6 and 12 hours, 6 hours, 3 hours and 2 hours respectively. The heating and

Table 3.5: Green Densities

Nomenclature	Green Density (gm/cc)
1A	2.26
1B	1.98
1BX	2.21
1F	2.01
1FX	2.24
1G	2.21
2G	2.12
3A	2.06
AFA	2.28
AFB	2.23
AFC	2.26
B2A	2.32
B2B	2.33
B2C	2.33
CA	2.32
CB	2.32
CAA	2.26
CAB	2.31
CuA	2.26
CuBX	2.21
CuB	2.21
CuC	2.31
CuD	2.30
CuE	2.30

Continued...

Table 3.5 continued.

Nomenclature	Green Density (gm/cc)
FA	2.21
ZnA	2.29
ZnB	2.28
MgA	2.18
MgB	2.26
MnA	2.21
MnAX	2.28
MnB	2.32
K	2.32
T	2.23
AS	2.29

cooling rates were gradual, the range being 20 - 120°/hour. The cooling rate was controlled right down to about 200°C in the globar furnace and the refractory kiln runs and in the case of the gas fired runs (1500° and 1600°) the cooling was controlled till about 1200°C and the furnace was shut down and the products were furnace cooled. A bedding of alumina powder ~ 100 # size was used to prevent the samples from adhering to each other.

The temperature measurements were carried out by (i) Pt/Pt 10%Rh thermocouples in the globar furnaces and the gas fired (1600°C) furnace. In both the cases the temperature was fairly uniformly distributed throughout the firing zone and the variations were within the range of $\pm 20^{\circ}\text{C}$, (ii) by optical radiation pyrometers in the gas fired runs at 1500°C and here the distribution was not uniform and a variation of $\pm 50^{\circ}\text{C}$ could not be ruled out and (iii) by Pt/Pt. 10%Rh thermocouples in the refractory kiln (1450°C run) along with std. seger cones. The temperature variation was limited to $\pm 20^{\circ}\text{C}$.

3.2 PRODUCT TESTING AND CHARACTERIZATION

The fired pellets were tested for the following physical properties.

(i) Linear shrinkage (ii) Geometric density

(iii) Porosity and (iv) True density. The mullite was detected by X-ray diffraction techniques and optical microscopy. The yield of mullite was also calculated from X-ray data and in some selected cases the yield was also obtained from the weight of the residue after leaching with hydrofluoric acid.

3.2.1 LINEAR SHRINKAGE

Linear shrinkage was measured as the ratio of the difference in diameters before and after firing to that before firing and is expressed in percent. Thus,

$$\text{Linear Shrinkage} = \frac{D_o - D}{D_o} \times 100$$

where, D_o = Diameter before firing, cms

and D = Diameter after firing, cms.

3.2.2 GEOMETRIC DENSITY

This was found as the weight to volume ratio of the various pellets. This gives the value of apparent density since the volume calculated from the diameter and thickness values includes porosity.

$$\text{Geometric Density or Apparent Density} = \frac{W_{\text{Dry}}}{\frac{\pi D^2 T}{4}}$$

where, W_{Dry} = Dry weight of the pellet - gms
 D = Diameter of the pellet - cms
 T = Thickness of the pellet - cms.

3.2.3 POROSITY

The porosity was measured in the usual manner prescribed. The pellets were weighed dry and then boiled in water for 2-3 hours. After boiling, the pellets were removed, dabbed lightly to remove water on the surface and weight of the soaked pellet was determined. The soaked pellet then was immersed in water and weighed. The porosity, which refers to open pores only is given as,

$$\text{Porosity} = \frac{W_S - W_D}{W_S - W_s}$$

where, W_D = Wt. of dry pellet - gms
 W_S = Wt. of soaked pellet - gms
 W_s = Wt. of immersed pellet - gms.

3.2.4 TRUE DENSITY

The nearly true density of the produced was derived from the dry weight and the porosity values as

$$\text{Density} = \frac{W_D}{W_D - W_s}$$

as $W_D - W_S$ gives the value of nearly true volume. In all the physical property measurements a single representative sample was taken which was free of cracks. The diameter and thickness measurements were done at 4 places each on each sample using a vernier caliper (Least count = 0.02 mm). The average of the value of the diameter and thickness was finally taken up for the respective calculations.

The above physical properties are given in Tables 3.6 to 3.10.

3.2.5. DETECTION OF MULLITE

3.2.5.1 X-ray Diffraction Studies:

The mullite formed in the products were initially detected by X-ray diffraction methods. Diffractometer tracings were obtained and characteristic peaks for mullite and any other phases present were looked for. The details of the X-ray investigations are furnished along with the tables providing the d and I values (Ref. Tables 3.11 to 3.13). The major phases observed are (i) mullite and (ii) alumina (α -alumina).

The amounts of mullite were calculated from the diffractographs, considering that only two phases are present. The wt. percent of mullite is obtained as ⁷⁶.

$$X_{\text{Mullite}} = \frac{1}{1 + k \frac{I_{\text{Corundum}}}{I_{\text{Mullite}}}}$$

$$\text{where, } k = \frac{I_{\text{Mullite}} (50\%)}{I_{\text{corundum}} (50\%)} = 1.7$$

These values are erroneous but not far from realistic since glassy phase has also been observed by chemical methods.

3.2.5.2 Optical Microscopy and Photomicrography:

Selected samples were polished in a sequential manner starting from Emery belts (120 grit) through silicon carbide powders 120, 240, 400, 600 and 800 grits and later with 1 micron alumina suspension for 24 hours and 1 μ diamond paste for about an hour for each sample. But, however, the contrast was indeed poor and the photographs do not practically reveal any data about the size or shape of the mullite crystals.

For an observer, however, a clear view of tiny glass like specks embedded in a foamy matrix is quite visible as usually seen in sintered mullite ceramics.

The photomicrographs were obtained with 300X magnification, reflected light on a 35 mm low speed film. The enlarged prints are given in plates 1 - 10.

3.2.5.3 Chemical Leaching with Hydrofluoric Acid:

The usual chemical method of quantitative determination of mullite is based on the solubility differences between mullite and the other glassy phases in hydrofluoric acid. The method adopted in the present study is as formulated by Joshi et al⁷⁷. The well produced mullite samples < 200 ~~#~~ was weighed out (about 0.5 gms) exactly into a platinum crucible, 10 ml of HF (48%) and 10 ml of 1:3 H₂SO₄ were added. The crucible was then heated on a water bath for 3-4 hours with occasional stirring. Then the solution is filtered off through a Whatman 42 filter paper on a polythene funnel 10% HF and HF acidulated water followed by distilled water were used for washing the residue in the same sequence. The precipitate was then ignited for constant weight and the mullite content was expressed in percentage as the ratio of residue to the weight of the sample taken, initially (see Table 3.14).

3.2.6 MODULUS OF RUPTURE

The modulus of rupture (M.O.R.) of some selected compositions were obtained at room temperature. The respective mixes were moulded into bars of 6" x 1½" x 1" under 5000 kg load. They were then air dried and fired on the refractory kiln (1450°C, 6 hrs soaking, 5 day cycle).

The length, breadth and depth of the fired bars were then measured and these bars were then broken under a three point loading in an Avery UTM m/c. The load required to break the bars were noted. The value of the M.O.R. is then obtained as,

$$\text{M.O.R.} = \frac{3WL}{2bd^2}$$

where W = load in kg

L = span length - cm

b = breadth - cm

d = depth - cm

The highest values of the M.O.R. obtained are to be considered nearer to the true values since the lower values were obtained from samples which had cracks on them. The bars with additions of CuO as CuSO_4 have been fired to 1450°C for only one hour in the laboratory gas fired furnace (Ref. Table 3.15 for details).

Table 5.6: Physical Properties of Mullite Product

$D_0 = 2.812$ cm; Temperature = 1400°C ; Time of soaking = 6 hrs.

Nomenclature	Shrinkage percent	Porosity percent	Geometric Density gm/cc	True Density gm/cc
1a	2.42	22.71	2.31	2.90
1b	4.02	32.15	2.94	2.97
1c	3.28	21.30	2.26	2.92
1d	2.92	22.6	-	2.96
2a	2.92	24.45	2.21	3.02
2b	2.48	24.42	2.32	3.13
2c	3.30	28.71	2.11	3.08
2d	5.48	33.61	1.99	3.09
2e	6.62	38.99	1.86	3.16
2f	7.76	41.15	1.80	3.15
3a	13.45	22.7	2.04	2.95
3b	13.59	29.24	-	2.91
Th	4.2	21.03	2.45	3.14
B_2O_3	4.16	12.79	2.29	2.65
C	3.56	20.49	2.28	2.95
Cu	1.91	19.90	2.24	2.89
Mn	1.64	24.71	2.17	2.94
Mg	1.85	22.51	2.19	2.86
Zn	4.27	23.43	2.37	3.13

Table 3.7: Physical Properties of the Mullite Product

$D_0 = 2.664$ cm; Temperature = 1400°C ; Time of soaking = 12 hrs.

Nomenclature	Shrinkage percent	Porosity percent	Geometric Density gm/cc	True Density gm/cc
1A	1.501	23.855	2.19	3.00
1B	4.879	28.710	2.03	3.01
1BX	4.654	19.301	2.35	3.02
1E	3.003	30.838	2.00	3.07
1EX	2.777	17.543	2.25	2.93
1F	2.327	26.274	2.04	3.03
1FX	2.477	19.088	2.26	2.97
1G	3.303	19.983	2.33	3.01
2G	3.978	25.177	2.17	3.09
3A	15.540	25.592	2.09	3.11
FA	1.276	24.609	2.18	3.02
ZnA	0.525	26.522	2.11	2.99
ZnB	0.525	26.109	2.14	3.02
MgA	1.501	28.168	2.16	3.13
MgB	1.351	23.160	2.18	2.97
MnA	3.678	20.034	2.42	3.11
MnB	3.753	20.814	2.39	3.10
MnAX	2.702	22.563	2.31	3.15
MnBX	2.102	21.089	2.36	3.05
CuA	0.675	25.570	2.14	2.99
CuB	1.126	26.133	2.15	3.07
CuC	1.501	21.069	2.27	2.95
CuD	1.726	20.361	2.23	2.96
CuE	1.951	19.918	2.27	2.94
CuBX	0.900	23.722	2.17	2.96
CAA	1.576	21.704	2.07	2.95
CAB	1.651	20.923	2.21	2.95
CAC	1.876	19.511	2.12	2.92
CAO	2.027	23.470	2.21	2.96
B2A	5.030	17.915	2.45	3.16
B2B	5.180	14.349	2.53	3.07
B2C	5.330	13.539	2.58	3.07
AA	2.477	21.342	2.28	3.05
AFB	2.177	24.071	2.26	3.08
AFC	1.876	26.619	2.19	3.11
CA	3.678	18.557	2.37	3.07
CB	2.852	15.465	2.31	2.89
K	3.528	23.922	2.43	3.28
TiA	0.600	28.154	2.12	3.10

Table 3.3: Physical Properties of the Mullite Product

$D_0 = 2.664$ cm; Temperature = 1500°C ; Time of soaking = 3 hrs.

Nomenclature	Shrinkage percent	Porosity percent	Geometric Density gm/cc	True Density gm/cc
1A	3.753	18.176	2.43	3.10
1B	7.282	22.323	2.16	3.01
1BX	4.204	15.803	2.38	2.87
1E	6.831	19.952	2.26	3.01
1EX	3.228	18.873	2.32	2.97
1F	4.129	22.078	2.29	3.03
1FX	2.777	21.221	2.30	3.01
1G	2.327	24.217	2.22	3.11
2G	3.153	22.163	2.30	2.99
3A1 ^a	18.168	20.375	2.24	3.09
3A2 ^a	20.345	9.671	2.54	2.92
3B1 ^b	19.594	7.977	2.38	2.95
3B2 ^b	21.096	4.080	3.09	2.89
FA	1.876	24.365	2.23	3.03
ZnA	1.576	25.047	2.44	3.00
ZnB	1.126	23.861	2.17	3.00
MgA	1.651	23.996	2.23	3.02
MnA	3.153	21.489	2.21	3.01
MnB	2.852	20.213	2.09	3.11
CuA	1.951	21.781	2.23	2.98
CuB	2.252	20.978	2.12	3.04
CuC	2.102	20.831	2.23	2.98
CuD	2.477	18.629	2.29	2.94
CuE	2.102	19.700	2.25	2.91
CuBX	2.252	25.541	2.12	3.03
CAA	2.102	20.309	2.18	2.91
CAB	2.477	13.650	2.25	2.78
CAC	3.003	12.270	2.28	2.74
CAO	2.702	19.860	2.27	2.94
B2A	1.876	21.054	2.26	2.96
B2B	2.477	19.114	2.27	2.91
B2C	2.552	15.729	2.27	2.89
AFB	0.900	27.866	2.15	3.09
K	1.951	23.097	2.23	2.99
CB	2.777	15.349	2.31	2.86
TiA	0.900	27.417	2.14	3.08
T	2.252	24.503	2.27	3.06

9 - 2 Samples of 5A

9 - 1 Sample of 13B

Table 3.9: Physical Properties of the Mullite Products

$D_0 = 3.244$ cm; Temperature = 1450°C ; Time of soaking = 6 hrs.
(Refractory kiln)

Nomenclature	Shrinkage percent	Porosity percent	Geometric Density gm/cc	True Density gm/cc
M1	2.281	37.981	1.93	3.21
M2	2.589	34.459	1.99	3.09
M2A	0.493	35.935	1.94	3.12
M21	4.747	27.929	2.10	2.98
M22	3.020	31.750	2.02	3.00
M2A1	3.267	30.387	2.06	3.01
M2A2	0.739	34.239	1.95	3.01
MLX	5.610	26.443	2.19	3.03
MLX1	6.226	24.184	2.22	3.00
MLX2	4.747	27.109	2.15	3.04
FA	1.787	29.665	2.21	3.24
FM	0.246	33.563	2.09	3.24

Table 3.10: Physical Properties of the Mullite Product

$D_o = 2.536$ cm; Temperature = 1600°C ; Time of soaking = 2 hrs.

Nomenclature	Shrinkage percent	Porosity percent	Geometric Density gm/cc	True Density gm/cc
M1	3.391	28.38	2.15	3.17
M2	4.495	27.62	2.18	3.06
M1A	1.419	30.53	2.08	3.10
M2A	2.650	30.65	2.05	3.06
M11	6.760	24.60	2.20	3.05
M21	6.720	22.45	2.28	2.96
M22	4.810	25.10	2.31	2.98
M2A1	6.040	21.80	2.27	2.98
M2A2	3.020	29.20	2.10	3.05
M1X	7.460	20.60	2.33	2.97
M1X1	7.710	17.05	2.39	2.94
M1X2	6.720	20.00	2.29	3.02
FM	2.710	25.75	2.23	3.12
FA	3.76	17.72	2.31	3.04

Table 3.11: X-ray Data Samples Fired at 1400°C for 6 hrs

d Å	3.48	3.43	3.39	2.69	2.54	2.29	2.21	2.12	1.74	1.59	1.52	Mullite content percentage
Phase	M	M	M	M	M, A	M, A	M	M	A	A	M	
Sample												
1a	-	-	10	3.7	4.6	0.9	3.5	1.6	1.3	0.6	3.1	80.3
1b	-	-	10	4.7	5.4	1.5	4.8	1.7	1.2	0.6	3.1	81.2
1c	-	-	10	3.2	3.9	1.0	3.2	1.8	1.5	0.7	2.7	79.6
1d	-	-	10	3.2	4.3	0.9	3.3	1.8	1.5	0.6	-	79.6
2a	1.8	-	10	5.0	8.0	3.6	7.3	2.8	4.7	2.2	6.8	57.4
2b	-	-	10	3.6	12.0	1.5	3.0	2.1	4.5	2.3	3.8	58.0
2c	-	-	10	3.8	13.9	0.9	5.1	1.5	4.4	1.7	6.6	54.0
2d	2.8	-	10	3.4	11.0	1.6	5.5	1.9	3.6	1.9	7.9	61.6
2e	2.4	-	10	3.0	11.0	1.8	5.1	3.5	3.8	1.4	6.8	62.7
2f	2.0	-	10	3.6	9.5	1.3	5.9	4.1	2.0	0.9	5.0	75.0
3a	-	-	10	3.4	6.3	2.3	7.1	2.2	1.8	0.9	3.7	74.5
3b	5.6	-	10	2.9	22.0	1.6	5.1	2.0	9.1	5.1	19.8	39.0
B ₂ O ₃	1.1	-	10	3.5	4.7	1.0	3.2	1.9	1.3	0.6	3.2	80.0
G	-	-	10	3.4	11.0	0.8	4.0	1.8	3.4	1.6	7.3	63.4
Cu	-	-	10	3.3	3.5	0.9	2.8	2.2	1.9	0.5	2.3	75.7
Mg	-	-	10	3.8	3.2	0.9	3.0	2.8	1.1	0.4	2.1	85.0
Mn	-	-	10	3.2	2.7	0.8	2.9	1.9	0.6	0.3	1.7	89.1
Zn	3.5	-	10	3.2	15.4	1.1	3.8	1.6	5.1	2.7	10.8	53.5

M = mullite A = Alumina (α -Al₂O₃)

Table 3.12: X-ray Data Samples Fired at 1400° for 12 hrs

d	A	3.49	3.43	3.33	2.69	2.54	2.29	2.21	2.12	2.03	1.74	1.59	1.52	Mullite content percentage
Phase	M	M	M	M	M, A	M, A	M, A	M	M	A	A	A	M	
Sample														
1A	5.7	5.9	10	2.1	7.9	1.1	4.7	1.1	5.3	2.6	1.1	1.6	50.4	
1B	-	1.5	10	3.3	6.7	1.5	5.5	2.2	1.5	6.8	3.5	3.7	79.7	
1BX	1.5	4.8	10	3.3	5.6	1.0	3.5	1.7	2.1	1.0	4.0	2.3	73.6	
1F	-	5.9	10	3.5	4.1	1.2	3.6	1.3	0.7	6.3	2.4	2.3	89.0	
1G	1.3	5.4	10	3.1	5.8	1.2	3.5	1.4	1.5	0.6	3.5	2.1	79.3	
2G	-	5.5	10	3.1	2.6	0.7	3.0	1.4	-	-	0.9	1.9	97.5	
3A	0.5	6.3	10	3.7	5.7	1.5	5.2	1.5	0.7	0.2	1.3	2.3	90.2	
3B	-	5.4	10	3.2	5.7	1.9	5.9	2.1	0.7	-	2.6	2.2	89.3	
CA	3.6	6.4	10	3.3	11.2	0.9	4.1	1.1	3.6	3.3	9.5	3.3	62.7	
B2A	3.1	3.1	10	4.0	21.1	1.7	4.5	1.7	3.7	4.0	14.3	3.3	47.0	
B2C	-	5.0	10	3.3	18.3	1.7	4.3	1.7	3.7	3.3	14.3	3.3	40.5	
CAC	0.8	5.5	10	2.5	3.8	0.8	2.3	1.7	0.5	0.3	2.6	2.2	90.4	
CAA	-	5.8	10	3.3	6.4	0.7	2.9	1.8	1.7	0.1	1.3	2.6	92.7	
CAB	1.9	6.0	10	3.7	7.6	-	2.8	1.5	2.0	1.3	5.0	2.4	79.6	
CAC	2.4	5.9	10	4.3	18.7	1.0	4.0	1.3	5.3	2.0	11.3	2.0	74.3	
MnA	4.0	8.0	10	3.0	7.4	1.2	3.6	1.6	2.2	1.2	4.6	2.4	57.5	
MnB	1.8	6.0	10	3.4	7.4	0.8	2.6	1.8	0.2	-	1.7	2.4	72.8	
MgA	-	6.0	10	3.9	2.6	0.6	2.5	1.7	0.4	0.4	1.7	2.1	60.2	
MgB	-	7.1	10	3.0	2.9	0.8	2.6	1.8	0.6	0.2	1.9	2.1	91.4	
CuA	0.9	5.4	10	3.3	3.0	0.8	2.6	1.5	0.5	0.3	1.5	2.2	92.1	
CuG	0.5	5.1	10	3.3	2.8	0.6	2.6	1.6	0.6	0.4	1.7	2.1	91.2	
CuE	0.7	5.7	10	3.1	3.0	0.7	2.2	1.4	0.2	-	1.1	2.0	96.2	
ZnA	-	5.5	10	3.2	2.5	0.7	2.3	1.4	0.2	-	1.2	1.7	96.2	
ZnB	-	5.9	10	3.4	2.4	0.7	2.3	1.9	1.2	0.5	3.2	2.4	83.6	
AFA	1.4	6.2	10	3.7	6.0	0.9	4.0	1.8	1.2	2.4	9.1	3.1	53.5	
AFB	3.8	7.1	10	3.6	13.6	1.1	4.0	1.9	5.1	2.4	5.3	2.6	66.2	
AFC	1.9	6.8	10	3.4	3.9	0.9	3.4	1.9	3.0	1.4	5.3	2.6	95.5	
FA	-	5.9	10	3.5	2.8	0.7	2.1	1.4	0.3	-	0.8	1.5		

Intensity, I

M = Mullite

A = Alurina (α -Al₂O₃)

Table 3.13: X-ray Data Samples Fired at 1500°C for 3 hrs

d Å	3.48	3.43	3.39	2.69	2.54	2.29	2.21	2.12	2.03	1.74	1.59	1.52	Mullite content percentage
Phase	M	M	M	M	M, A	M	M	A	A	A	A	M	
Sample													
2G	-	6.0	10	3.7	1.9	0.8	2.5	1.8	0.1	-	0.9	2.3	38.3
3B	6.0	5.6	10	2.8	13.2	1.2	4.3	1.2	6.4	3.2	3.4	3.2	47.8
CuA	-	7.7	10	4.7	2.9	1.2	3.6	2.6	0.1	-	1.4	3.0	99.0
MgA	-	5.2	10	3.2	2.0	0.9	2.2	1.4	1.2	-	1.2	2.0	83.0
MnA	-	5.2	10	3.2	2.0	0.7	2.3	1.5	0.1	0.1	0.9	2.0	97.8
ZnB	-	5.5	10	3.3	2.0	0.7	2.5	1.7	0.1	-	1.1	2.1	98.0
Samples Fired at 1450°C for 6 hrs (Refractory kil)													
M1A	0.3	5.7	10	3.9	7.6	1.9	6.7	2.3	0.9	0.3	2.3	4.3	87.2
M1A1	-	5.6	10	4.2	5.3	1.4	7.0	2.5	0.8	0.3	2.5	4.2	88.0
M1A2	-	5.7	10	4.0	5.7	2.0	7.3	2.7	0.3	-	2.7	5.3	95.2
A = Alumina (α -Al ₂ O ₃)													
M = Mullite													

Table 5.14: Quantitative Analysis of Mullite

Nomenclature	Temperature Time of Sintering	Yield percent (Chemical) a	Yield percent (Chemical) Corrected $a \times 100/90$	Yield percent (X-ray)
1a	1400/6	56.42	62.69	80.3
1a	1400/12	59.70	66.33	50.4
1a	1500/3	54.54	60.60	-
Zn	1400/6	61.05	67.83	53.5
ZnA	1400/12	66.72	74.13	96.2
ZnB	1400/12	70.56	78.40	96.2
ZnB	1500/3	73.40	81.56	98.0
Cu	1400/6	64.53	71.70	75.7
CuA	1400/12	69.05	76.72	91.4
CuC	1400/12	73.62	81.80	92.1
CuE	1400/12	68.02	75.58	91.3
CuE	1500/3	65.51	72.79	-
Mn	1400/6	68.63	76.26	85.0
MnA	1400/12	69.52	77.24	57.5
MnB	1400/12	72.65	80.72	72.8
Std. fused mullite	(99% plus purity)	85.72	95.24	-

Table 3.15: Modulus of Rupture at Room Temperature

$$M.O.R. = \frac{3WL}{2bd^2} \quad L = 11.43 \text{ cm}$$

Nomenclature		d cm	b cm	W Kg	M.O.R. Kg/cm ²
M1A	(i)	2.333	3.671	125	107.25
55 clay/45 A = 2	(ii)	2.322	3.658	135	117.35
	(iii)	2.344	3.662	163	138.90
M2A	(i)	2.305	3.598	90	80.70
57 clay/43 A = 2	(ii)	2.365	3.600	100	85.15
M1A1		2.366	3.613	225	190.75
55 clay/45 A = 2					
1.045MgCO ₃					
M1A2		2.400	3.658	215	174.95
55 clay/45 A = 2		2.402	3.665	190	154.50
0.5ZnO					
M1		2.201	3.407	80	83.10
55 clay/45 Malco		2.402	3.407	105	110.70
M2		2.192	3.376	93	98.30
57 clay/43 Malco		2.207	3.369	109	113.90
M11		2.202	3.391	166	173.20
55 clay/45 Malco		2.252	3.388	81	80.80
1.045MgCO ₃					

Continued...

Table 3.15 continued.

Nomenclature	d cm	b cm	W Kg	M.O.R. Kg/cm ²
M12	2.226	3.416	71	71.90
55 clay/45 Malco 0.5ZnO	2.216	3.423	114	116.25
M1AC ^φ	2.261	3.613	70	75.00
55 clay/45 A = 2 1.56 gm CuSO ₄ = 0.5 gm CuO				
M2AC ^φ	2.388	3.576	113	95.00
55 clay/45 A = 2 1.56 gm CuSO ₄	2.245	3.610	110	103.65
M2C ^φ	2.275	3.571	82	76.05
55 clay/45 A = 2 1.56 gm CuSO ₄	2.266	3.577	116	108.30

^φ Samples fired at 1450°C for 1 hr only.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 CLAY/ALUMINA RATIO

Using Kerala china clay and $\Lambda = 2$ alumina, the ratio of clay to alumina has been varied as follows: 45/55, 50/50, 55/45 and 57/43. Equivalent ratios to some of these above have been tried earlier by other investigators^{41,66,63}. The sintering conditions were 1400°C for 6 hrs, 1400°C for 12 hrs, 1450°C for 6 hrs, 1500°C for 3 hrs and 1600°C for 2 hrs. The furnaces employed for this purpose are already described in Chapter 3. The percentage of mullite obtained in the product is estimated by X-ray methods and is given in Tables 3.11 - 3.13 and plotted in Fig. 4.1. Percentage of mullite in the case of the 1A series (55/45 ratio) was also estimated by chemical analysis.

Chemical analysis consistently gave a much lower value than the X-ray method. However, for purposes of comparison of one sample with another, the X-ray method should be adequate, even though the absolute amount of mullite as revealed by X-ray data may be somewhat higher.

especially at lower firing cycles such as $1400^{\circ}\text{C}/6$ hrs densities as low as 2.90 gm/cc were obtained. This must be due to the volume expansion during the reaction as has been observed by other investigators or due to closed pores. Same sample sintered at a higher would become denser.

From Tables 3.6 to 3.10 it may be observed that the radial shrinkages were less than 5 percent and quite often about 2-3 percent. However the porosity in general was between 20-25 percent. The observed differences between the geometric density and the true density is consistent with this porosity. Most of the porosity appears to be due to open pores. While these higher values of porosity render these specimens unsuitable for applications such as substrates for resistors and other electronic components, the values are within the tolerance limits for super refractories and grog.

Samples 1a, 1c, and 1d of Table 3.6 are identical in composition (55 clay/45 Al_2O_3) except that the alumina was used as ~~received~~^{refined} in 1a and ground for 24 and 48 hrs in 1c and 1d. It may be observed that there is no marked benefit which could be realised, due to grinding even though the particle sizes generally shifts to somewhat smaller values. As a consequence all subsequent experiments were carried out with the alumina as received.

The modulus of rupture values (Table 3.15) show a marked decrease when the alumina content is reduced. There is a decrease to about 50 percent between 1A and 2G compositions (55/45 and 57/43 ratios). Three samples of 1A were tested and gave significantly different M.O.R. values. Since visible cracks were present with two samples that gave lower values only the maximum values available for each series is considered. In view of the small number of samples for which reliable results are available perhaps complete reliance can not be placed on the absolute values. However, the general trend that 2G has lower M.O.R. values than 1A appears to be the case. This is understandable since 2G has a higher mullite content than 1A and since mullite has a lower M.O.R. than alumina of comparable porosity.

4.2 SOURCE OF ALUMINA

While retaining the same china clay as one constituent, a number of different materials was used as sources of alumina. These include A = 2, A = 16 and Hydral 710 from ALCOA and Bayer Alumina from MALCO. The characteristics of these aluminas are listed in Table 3.2.

For a clay to alumina ratio of 55/45, gradual replacement of A = 2 by Hydral 710 in steps has not made much difference to the mullite formed at 1400°C (Fig. 4.2). On the other hand firing at 1400°C for 12 hrs gives 70 percent

mullite with 100 percent $\Lambda = 2$ and 80-90 percent mullite when $\Lambda = 2$ is partly or wholly replaced by Hydral. In both cases the enhanced reactivity of Hydral due to its small particle size must be an important factor.

In the case of 50 clay/50 alumina mixtures gradual replacement of Hydral for $\Lambda = 2$ steadily increased the percent mullite formed (Fig. 4.2).

The ratio of 25 clay/34 Hydral (3B) corresponding to a clay/alumina ratio of 57/43 yields densities of 2.91-2.95 gm/cc in the temperature range 1400-1500°C. On the other hand, 25 clay/39 Hydral (3A) (55 clay/45 alumina) yield densities up to 3.10 gm/cc at 1400-1500°C as shown in fig. 4.2. The higher density may be due to the presence of alumina in this composition.

It may be worth noting in Table 3.7 that the sample 3A has an unusually high shrinkage of 15.0, the inclusion of Al_2O_3 as Hydral appears to lead to higher porosities than when alumina is introduced as $\Lambda = 2$ except that most samples fired at 1500°C for 3 hrs have an unusually low porosity of 5-10 percent (Table 3.8). The shrinkage appears to increase as Hydral replaces $\Lambda = 2$ (Table 3.6 to 3.8). This may be attributed to loss of water from the Hydral.

Similarly $\Lambda = 2$ was partly replaced by $\Lambda = 16$ - a much finer and more reactive alumina than $\Lambda = 2$. In figs. 4.2 to 4.4 and Table 3.6 to 3.8, $\Lambda = 16$ appears to behave very much like Hydral. Shrinkage values are close to those of with $\Lambda = 2$ in addition and the porosity is again around 20 percent. Just as

in the case of Hydral, there is a progressive increase in the shrinkage values as the amount of $\Lambda = 16$ added increases. This may be indicative of the improved sintering due to the ^{small} particle size and reactivity of $\Lambda = 16$.

In 55/45 and 57/43 ratios $\Lambda = 2$ was replaced by Malco alumina. When this Malco alumina was super ground, it always showed a lower density, than when the alumina was not ground that fine (Tables 3.9 and 3.10)(Fig. 4.3). This might mean that Malco alumina aids mullite formation and the final densities of MIX fired at 1450° for 6 hrs and 1600°C for 2 hrs are close to the density of mullite, whereas the same composition but with a coarser Malco alumina yield densities close to 3.2 gm/cc. The higher density values indicate the presence of unreacted alumina. At clay to alumina ratios of 57/43 fired at 1450° for 6 hrs and 1600°C for 2 hrs, the densities obtained are essentially the same whether $\Lambda = 2$ or Malco Al_2O_3 is used. However the use of Malco alumina leads to unusually high porosities and low geometric densities (Tables 3.9 and 3.10). The large porosity may be attributed to the relatively coarser particle size of Malco alumina.

The modulus of rupture values in Table 3.15 show that for the ratio 55/45 the products with $\Lambda = 2$ and Malco as starting materials practically have the same values of M.O.R. whereas for the ratio 57/43 the Malco addition increases the M.O.R. value. The reason for this is not clear.

4.3 MINERALIZERS

4.3.1 COPPER OXIDE:

The ratio of 55/45 of clay/alumina was the base composition to which 0.5 to 2.5 percent CuO was added. CuO 0.5 and 1.0 percent as CuSO_4 solution was added to the base composition. At temperatures between 1400 and 1500°C all the CuO bearing compositions had much higher percent of mullite than without the mineralizer. The optimum addition for firing at 1400°C for 12 hrs appears to be about 1.5 percent (Ref. Fig. 4.5). The density of the samples are indicated in Fig. 4.6a, when fired at 1400°C for 6 hrs CuO does not seem to have any effect on the density. On the other hand, when fired at 1400°C for 12 hrs or 1500°C for 3 hrs a density of 3.05 gm/cc is reached at an optimum amount of 1.5 percent CuO. With the addition of CuO the shrinkage increases steadily and the porosity decreases. All the samples were coloured green, the colour getting darker as the amount of CuO added increases.

4.3.2 ZINC OXIDE

Zinc oxide is also as effective as copper oxide. The optimum percentage here seems to be about 1 percent. The density values as a function of the additive are shown in fig. 4.6a. The density seems to increase with percent

ZnO in the samples fired at 1400°C for 6 hrs. In the case of other firing conditions the change was not particularly significant. There is a marginal decrease of porosity with the addition with no significant change in shrinkage.

4.3.3 MANGANESE OXIDE

MnO is also as effective as ZnO and perhaps somewhat more effective than CuO. The density seems to be going through a maximum ~~at~~ 0.5 percent MnO added as the oxide or the sulfite but there is a minimum density observed on firing at 1500°C for 3 hrs. Only marginal changes in porosity and shrinkage are observed. The samples are coloured from pale pink to dark pink as the amount added increases.

4.3.4 MAGNESIUM OXIDE

The percentage of mullite obtained as per the X-ray data for 1 percent addition of MgO are 85.0 at 1400°C for 6 hrs, 60.2 at 1400°C for 12 hrs, 83.0 at 1500°C for 3 hrs and for 0.5 percent addition, 74.6 at 1400°C for 12 hrs and 88.0 at 1450°C for 6 hrs. The density, in general, decreases with MgO additions at all temperatures except it goes through a peak at 0.5 percent when fired at 1400°C for 12 hrs. There is a general decrease in porosity as the percentage of MgO increases. On adding MgO to

clay/alumina ($A = 2$) and clay/alumina (Malco) compositions the following observations are made.

A decrease in porosity with an increase in shrinkage and a decrease in density is also seen in samples fired at 1450°C for 6 hrs and 1600°C for 2 hrs when the clay/alumina ratio is 57/43 or 55/45 and the alumina used is either Malco or $A = 2$.

4.3.5 MISCELLANEOUS:

A number of other oxides and fluorides have been tried and the prominent of them being CaF_2 , B_2O_3 and AlF_3 . The variation of density with these additives at 1400°C for 12 hrs or 1500°C for 3 hrs is shown in fig. 4.6b. CaF_2 decreases the density with the amount of addition the decrease being steeper at 1500°C than at 1400°C . B_2O_3 tends to increase the density at 1400°C and decrease at higher temperature (at 1500°C). AlF_3 increases the density at 1400°C with increasing addition of AlF_3 . From Table 3.6 - 3.9 it is seen that in the case of CaF_2 and B_2O_3 with increasing additions the porosity decreases and shrinkage increases whereas in the case of AlF_3 the sequence is reversed. The X-ray data (Tables 3.11 - 3.13) reveal that the percentage of mullite found when 1 percent B_2O_3 is added is 47.0 at 1400°C for 12 hrs and with 3 percent B_2O_3 the percentage is

30.0 at 1400°C for 6 hrs and 40.5 at 1400°C for 12 hrs. The CaF_2 gives a decreasing mullite yield as the percentage increases at 1400°C for 12 hrs, 92.7, 79.6, 74.7 percent for 1, 2 and 3 percent CaF_2 additions. The AlF_3 additions give the following yield: 83.6, 56.5 and 66.2 percent for 1, 2, and 5 percent additions of AlF_3 .

4.3.6 ROLE OF MINERALIZERS:

In Section 1.5 the effect of mineralizers on mullite formation is reviewed. The main results are summarised in Table 1.2. A variety of additives have been tried. Each author gave his own sequence of effectiveness of these additives. The variables employed were the amount of additive temperature and soaking ^{time}. Of course each one has his own starting materials to supply Al_2O_3 and SiO_2 together with the impurities that these raw materials contain. It is therefore not surprising that a completely consistent picture can not be extracted from these data. In general the optimum amount of mineralizer for maximum mullitization varies from additive to additive and with temperature.

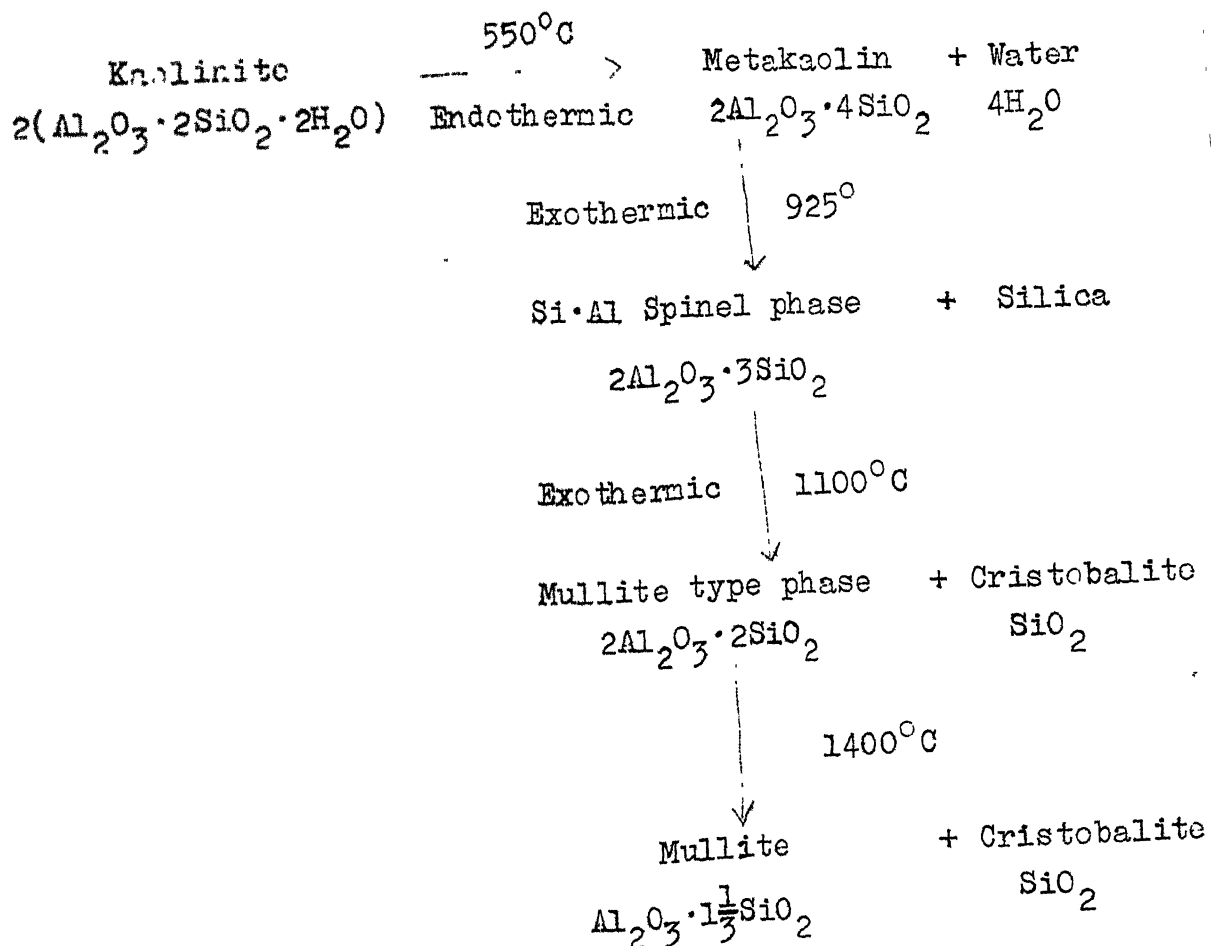
Moore and Prasad⁶⁸ pointed out that additions more than the optimum amount of mineralizer decrease mullite formation due to the breakdown of the mullite.

mullite phase into a glass and corundum rich phases. Another rationalisation is based on the field strength (ionic charge/ionic radius). Budnikov and coworkers^{64,70} pointed out that the smaller the field strength the more effective is the mineralizer. Avgustnik et al⁶⁷, Nazarenko et al⁶⁹, have disagreed with the above explanation based on field strength. McKenzie⁷⁵ agrees with the results of Avgustnik as far as the effect of alkali and alkali earth cations are concerned.

It is evident from the above that the role of mineralizers in mullitization remains in a confusing state inspite of the number of investigations carried out and the importance of mullite sintered at relatively low temperatures for technological uses. In the present study only those mineralizers were included which have been reported by most of the earlier workers to be atleast moderately effective. Therefore the differences observed from one mineralizer to another are not as great as would be the case if the mineralizers are randomly chosen. Of all the additives attempted only B_2O_3 , cryolite and AlF_3 do not have a positive effect on mullite formation under the conditions of the present investigation. The reason for this may be that at higher sintering temperatures and long soaking periods these materials might have volatilized off since no special precautions were taken to

minimise the vaporization. In the case of the other mineralizers there is an optimum amount for each set of sintering conditions.

According to Brindley and Nakahira³⁷ the reaction sequence of mullitization of kaolinite is as follows:



These studies show that (i) contrary to earlier belief that metakaolin is amorphous, it has considerable two-dimensional order with disorder in the third dimension.

ii) What used to ^{be} called γ - Al_2O_3 (after heating at 925°C) is now identified as a Si-Al spinel phase of composition $(\text{Si}_8)(\text{Al}_{10.67} \square_{5.33})_3\text{O}_{32}$ or $2\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$ where \square stands for an anion vacancy. The close packed planes of oxygen and hydroxyl ions in kaolinite, (001) plane, becomes the close packed planes of oxygen in spinel (111) plane, and finally the (310) plane of mullite, preserving the oxygen arrangement to a larger extent. Electron micrographs show the preserved arrangement of mullite needles with respect to the original kaolinite flakes. This suggests that the oxygen arrangement is preserved throughout the reaction sequence with cation diffusion causing the reaction.

In order to obtain single phase mullite enough alumina should be supplied from external sources to combine with the SiO_2 precipitated during the mullitization of kaolinite. The cationic diffusion which is the rate limiting step for the mullitization of kaolinite as well as for the combination of precipitated silica and added alumina suggests that the following factors should favour mullite formation from clay alumina mixtures; 1) Fine grained starting materials so that mixing is intimate and the diffusion paths short, (2) Presence of a liquid phase in which the cation diffusion coefficients are high, and (3) Point defects in particular

cation vacancies or interstitials which may enhance cation diffusion coefficients. The present as well as the earlier results may fit into place on the above basis.

The data presented in the present work would show that fine grained alumina such A = 16 and Hydral 710 are definitely more effective source of alumina than A = 2 or Malco aluminas. from the stand point of mullite formation. In fact the partial substitution of A = 2 by A = 16 or Hydral 710 has been shown to be useful.

In trying to establish the optimum clay/ Al_2O_3 ratio for mullite formation we started with compositions richer in alumina than the stoichiometric composition and ended with compositions which result in stoichiometric mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) after allowing for loss of SiO_2 by vaporization.

No liquid is expected at the temperatures employed in this investigation in this region according to phase diagram fig. 1.5. In making this statement no account is taken of the impurities present in the starting materials. It must however ^{be} recognised that some liquid formation is not unexpected in view of the chemical composition of the starting materials given in Table 3.1. Most of the mineralizers tried serve as fluxes and therefore the amount of liquid formed increases.

The amount of liquid formed is a function of the amount of mineralizer, sintering temperature, and in the case of transition metal oxides such as FeO, CaO, MnO etc. also of oxygen partial pressure. This can be deduced from the relevant phase diagrams. To consider the role of CaO on mullitization refer to portion of the $\text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{CaO}$ phase diagram shown in fig. 4.7. In the composition triangle $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 - \text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 - \text{SiO}_2$ a liquid is formed at a temperature of about 1380°C . The CaO content of the liquid is only about 10 percent with about 70 percent SiO_2 and 20 percent Al_2O_3 . Therefore even 1 percent addition of CaO would give rise to some liquid even at the lowest sintering temperatures employed namely 1400°C . With increase in temperature, the liquid content increases.

Fig. 4.8 gives a portion of the $\text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{MgO}$ phase diagram. In the mullite-cordierite - SiO_2 part of the system, the first liquid appears between $1400^\circ - 1450^\circ\text{C}$ and of approximately the composition $2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$ containing nearly 15 percent MgO. This suggests that there shall be some liquid formed with 1 percent additions of MgO at the firing temperatures employed, the increase in temperature increasing the liquid content. However in comparison with the CaO addition the liquid formation will be less for the same

amount of the oxide added.

Mn ions may exist in more than one oxidation state depending upon the oxygen partial pressure. Mn ions existing as MnO when the oxygen partial pressures are low form liquids at as low a temperature as 1200°C . In air Mn exists at a higher oxidation state as Mn^{3+} or Mn^{4+} , both of which have possibility of substituting for Al^{3+} . In such a case liquid formation is minimised.

In the case of iron oxide (fig. 4.9) two oxidation states of iron are possible; Fe^{2+} under reducing conditions or low oxygen partial pressures and Fe^{3+} in normal air atmosphere. In the former case liquid formation is quite considerable even at 1380°C whereas in the latter when no excess silica is present first liquid appears only at around $1450 - 1500^{\circ}\text{C}$ when the iron oxide present is around 30-40 percent. In the former case the iron ions are not absorbed into the lattice sites of mullite and corundum whereas in the latter a moderate amount is absorbed. This is the reason for the formation of more liquid in the presence of even small amounts of FeO at 1380°C than in the presence of greater amounts of Fe_2O_3 at higher temperatures (1460°C). The formation of liquid in the additions of Fe_2O_3 to the clay/alumina mixtures should hence be low compared to other additions of an equivalent amount.

While it should be ideally possible, from the phase diagrams, to estimate the amount of liquid formed as a function of the third component and temperature such quantitative estimates become difficult since we are no longer dealing with a three component system when one is using commercial raw materials with significant amount of impurities.

The photomicrographs do not clearly show the presence of glassy specs because of poor contrast. But however it was observed that there are tiny glassy specs distributed over the surface especially in the cases of CuO , MnO_2 , ZnO and MgO additions.

The third factor which has been cited to enhance cationic diffusion was point defects preferably cation vacancies. For this purpose, the cation of the mineralizer should be comparable to Al^{3+} or Si^{4+} ions in size. Further the coordination requirements of the mineralizer cation should be 4 or 6 as in the case of Si^{4+} and Al^{6+} . On this basis only Mg^{2+} , Fe^{3+} and Mn^{4+} have a chance of creating cation vacancies and may aid mullite formation. Many of the others such as Ca^{2+} , Cu^{2+} , Zn^{2+} etc. are too large to be accommodated in place of Al^{3+} or Si^{4+} .

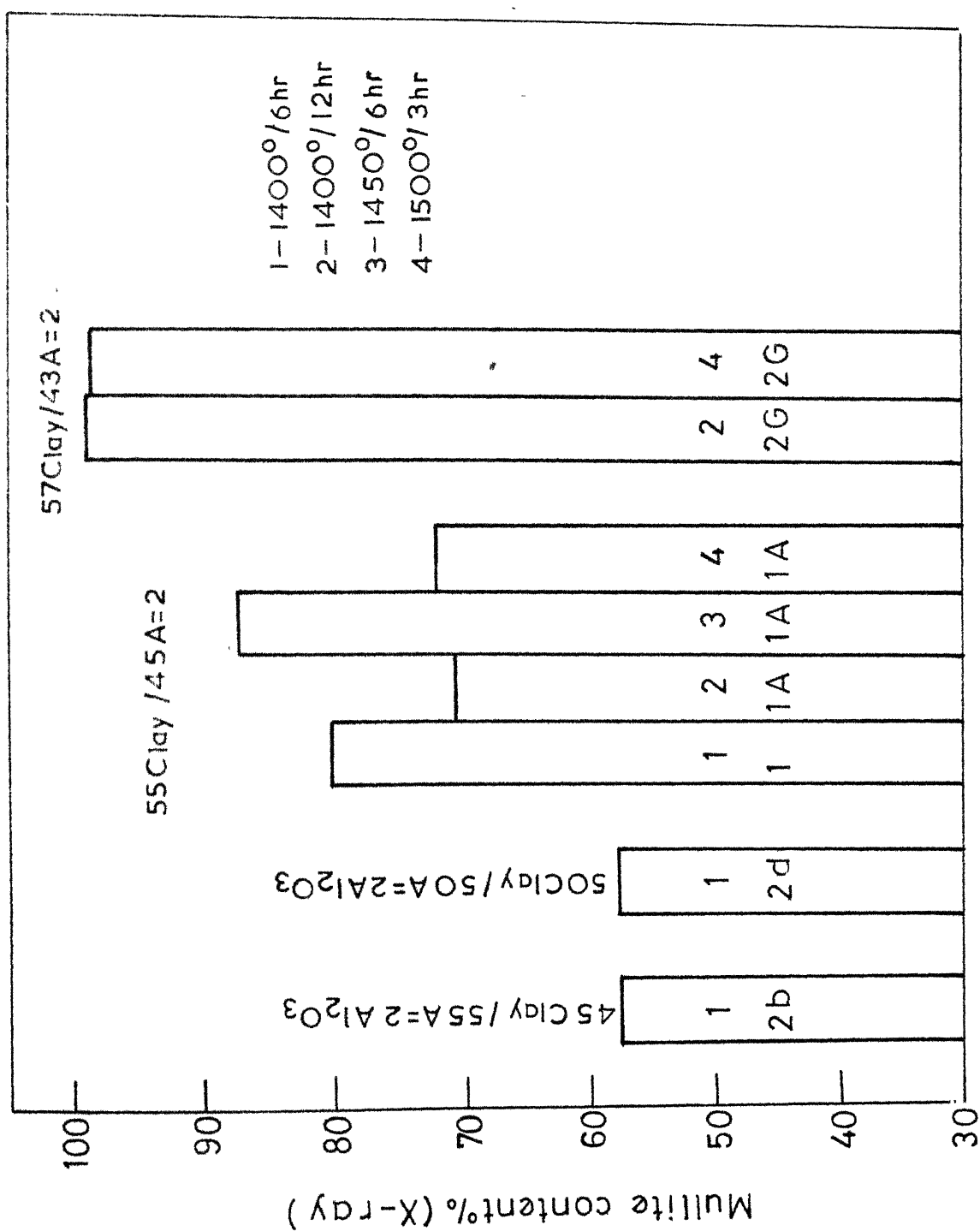


Fig.4.1 Mullite content vs. clay / alumina ratio

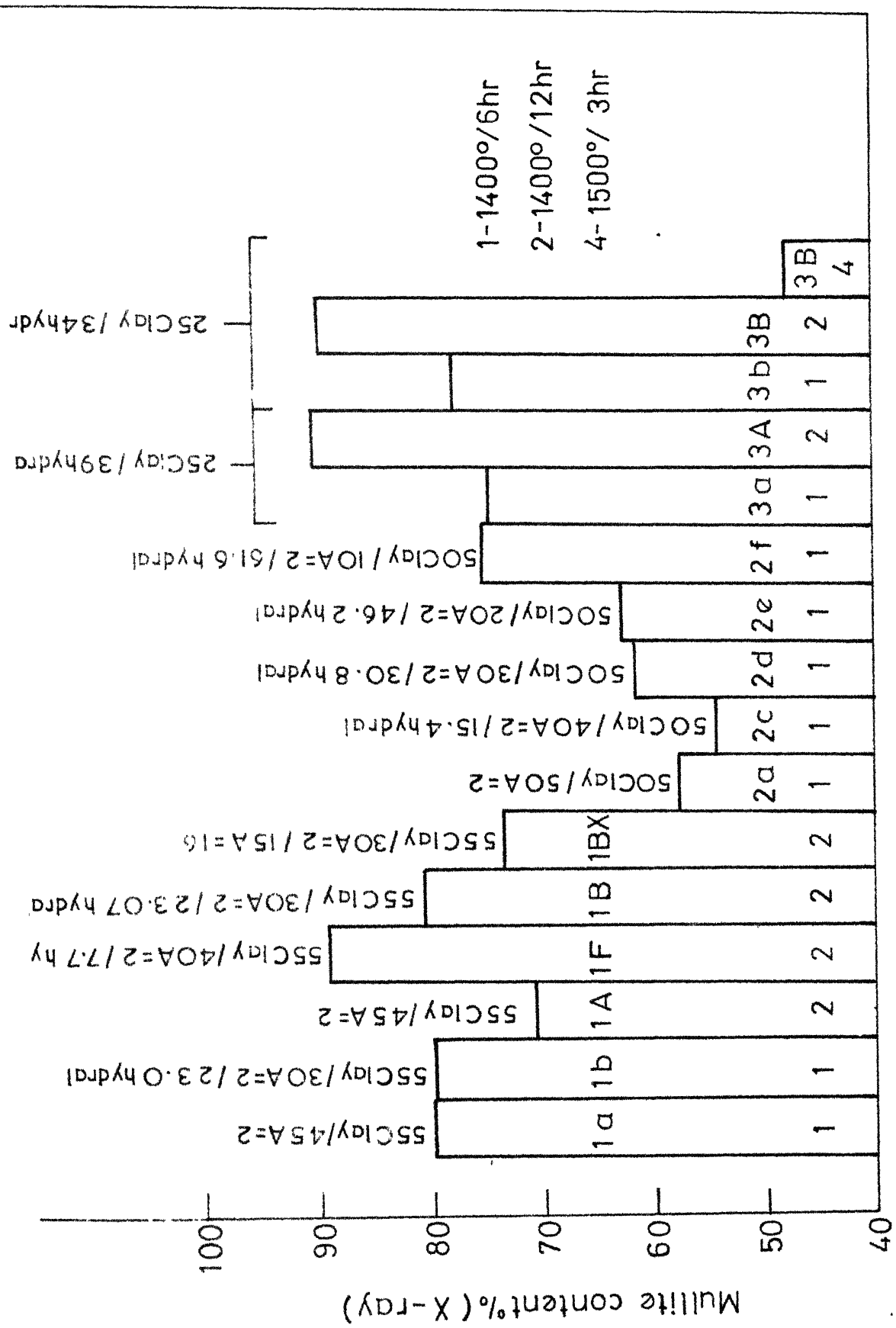


Fig. 4.2 Hydral / A=16 effect on mullite content

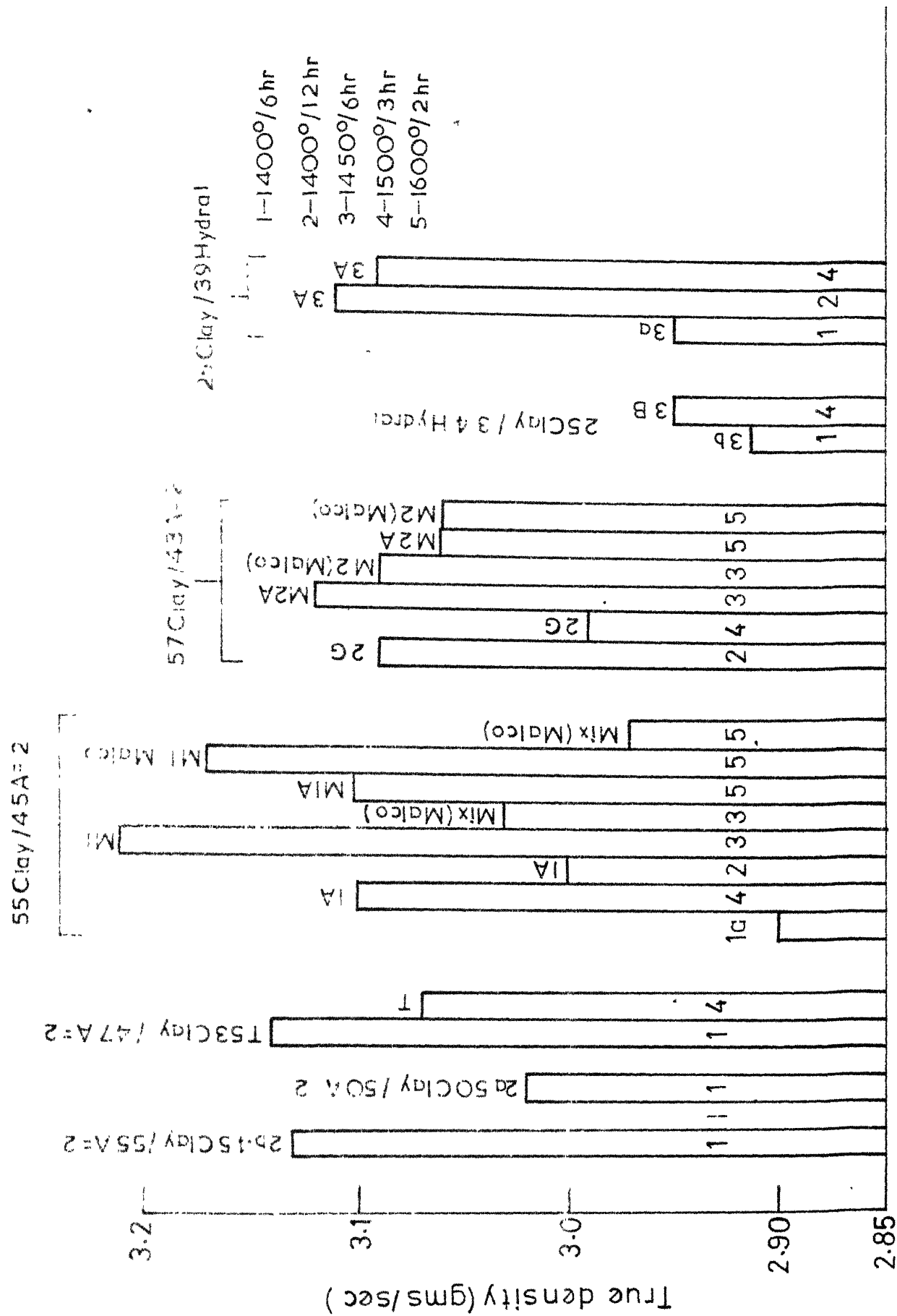


Fig. 4.3 Density vs. clay/alumina ratio

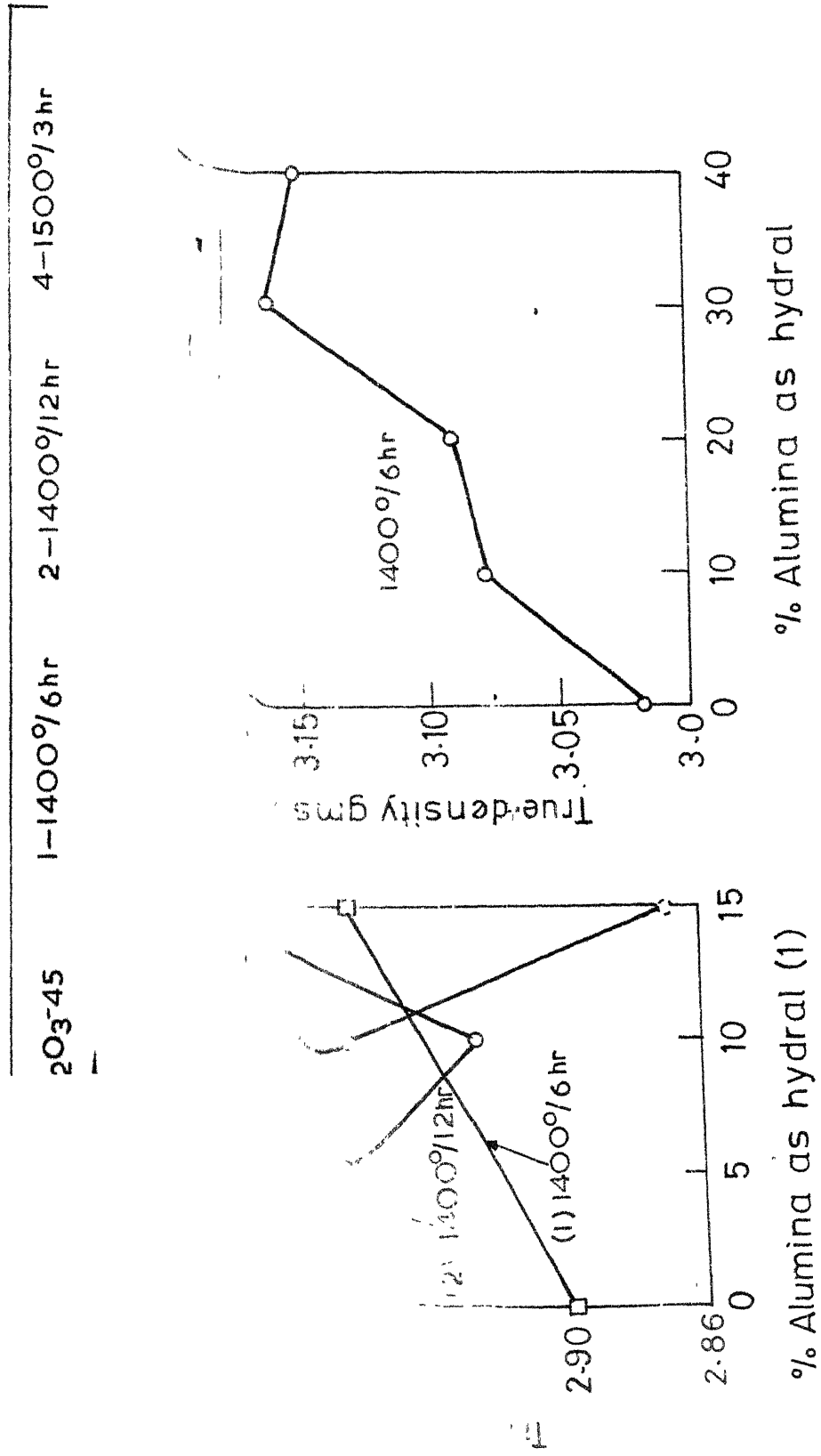


Fig. 4.4 Hydral/A = 16 addition vs. true density

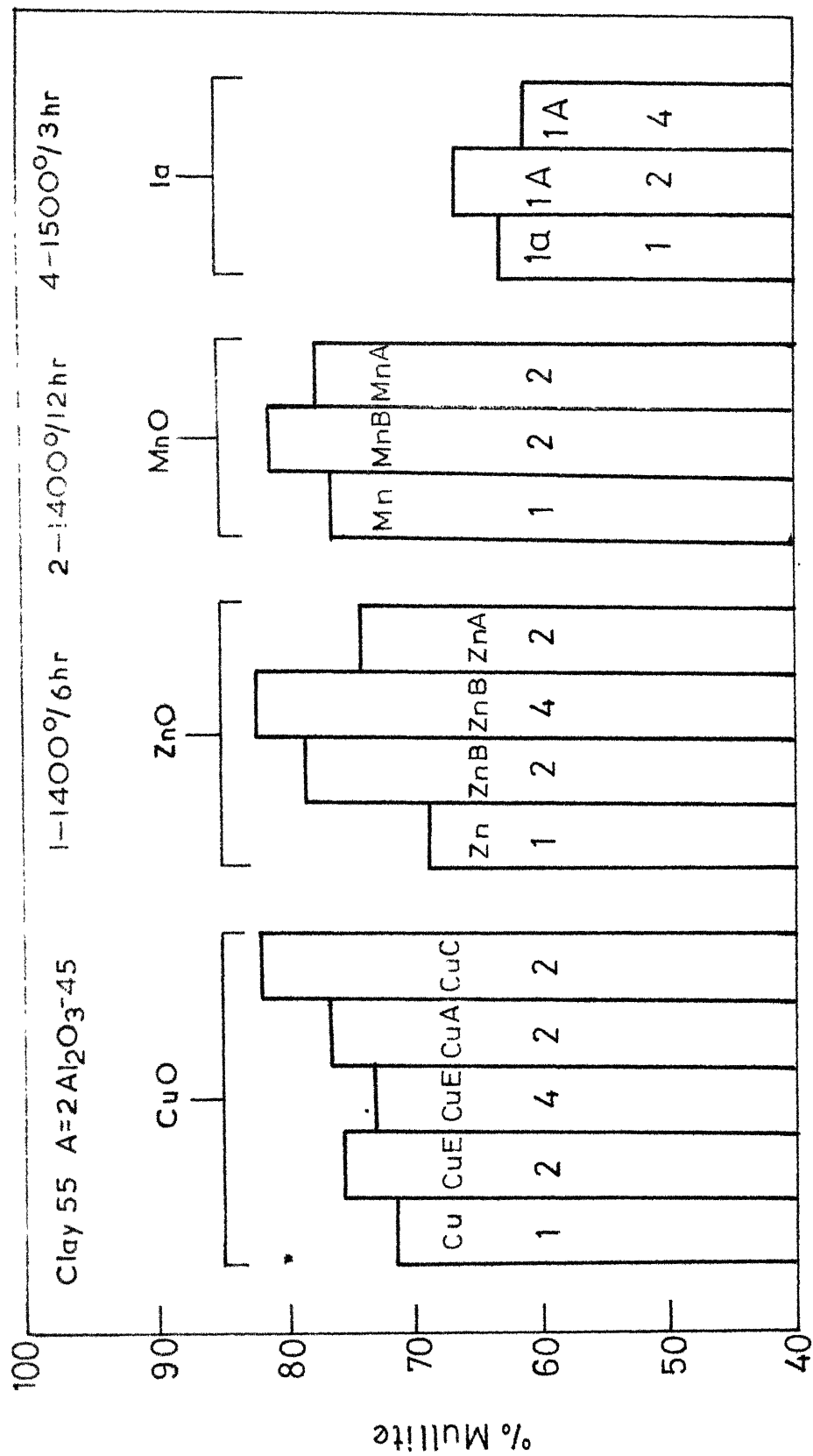


Fig.4.5 Mineralizer vs. yield of mullite (Chem.analysis)

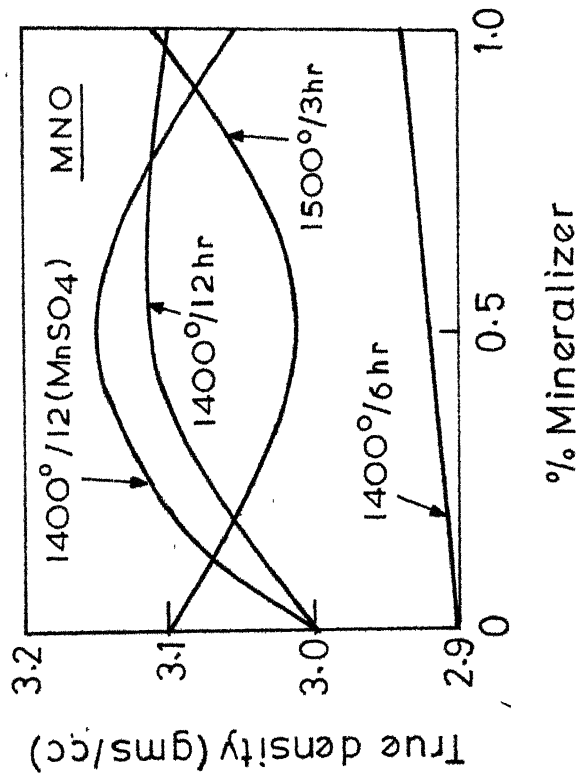
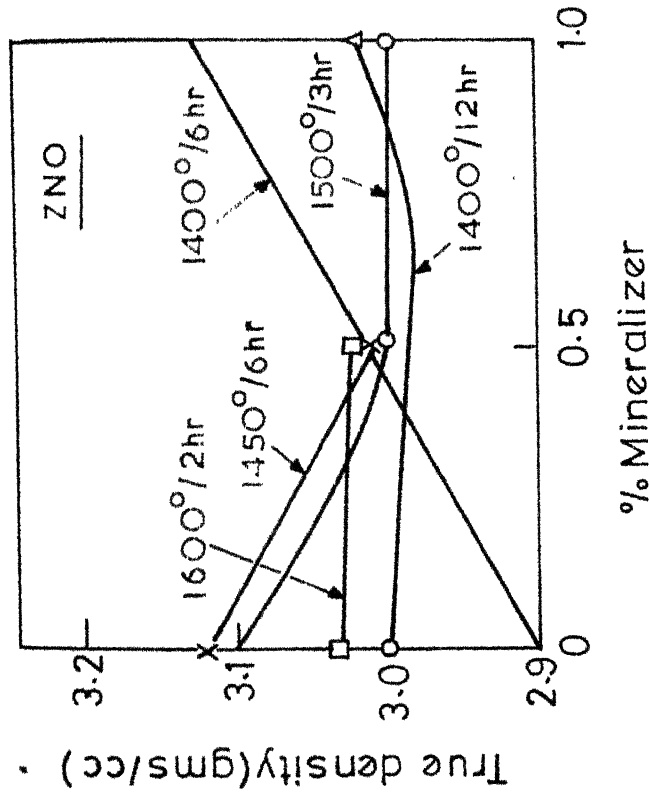
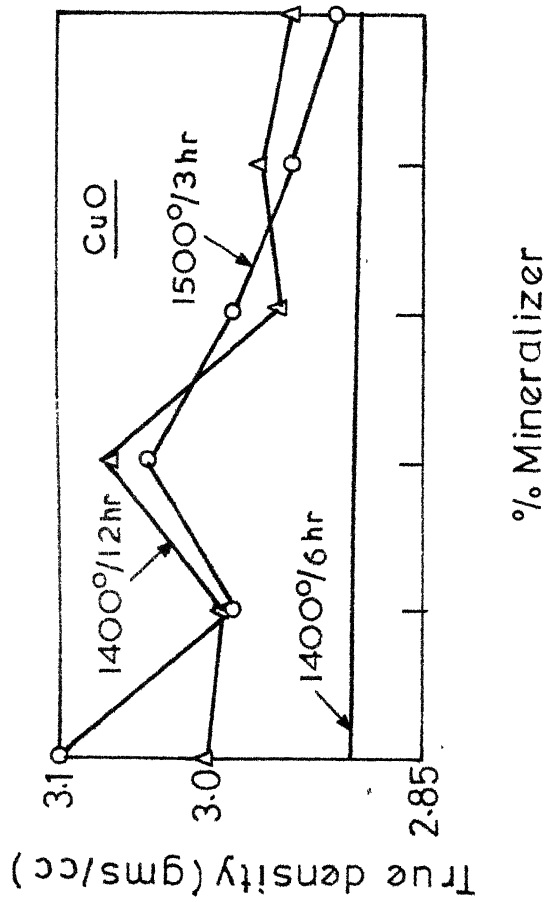
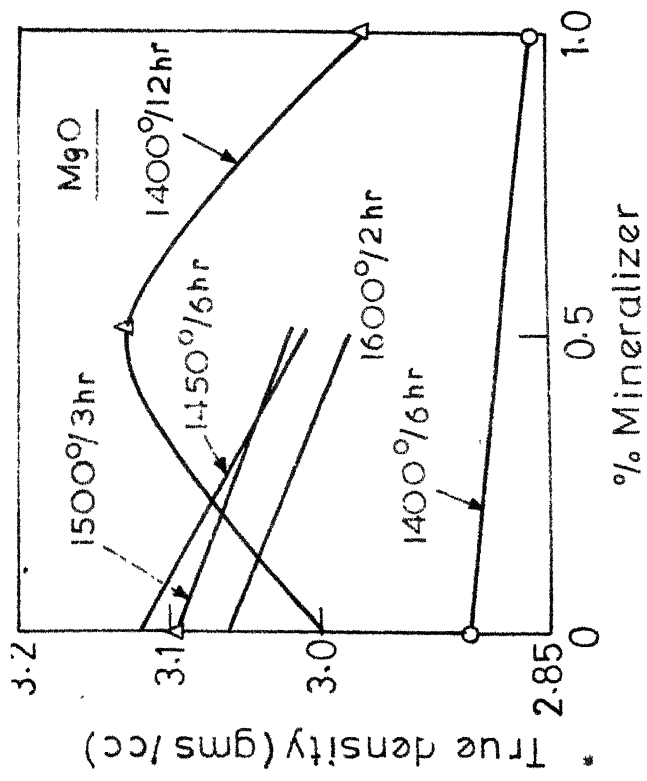


Fig.4-6a Mineralizer vs True density.

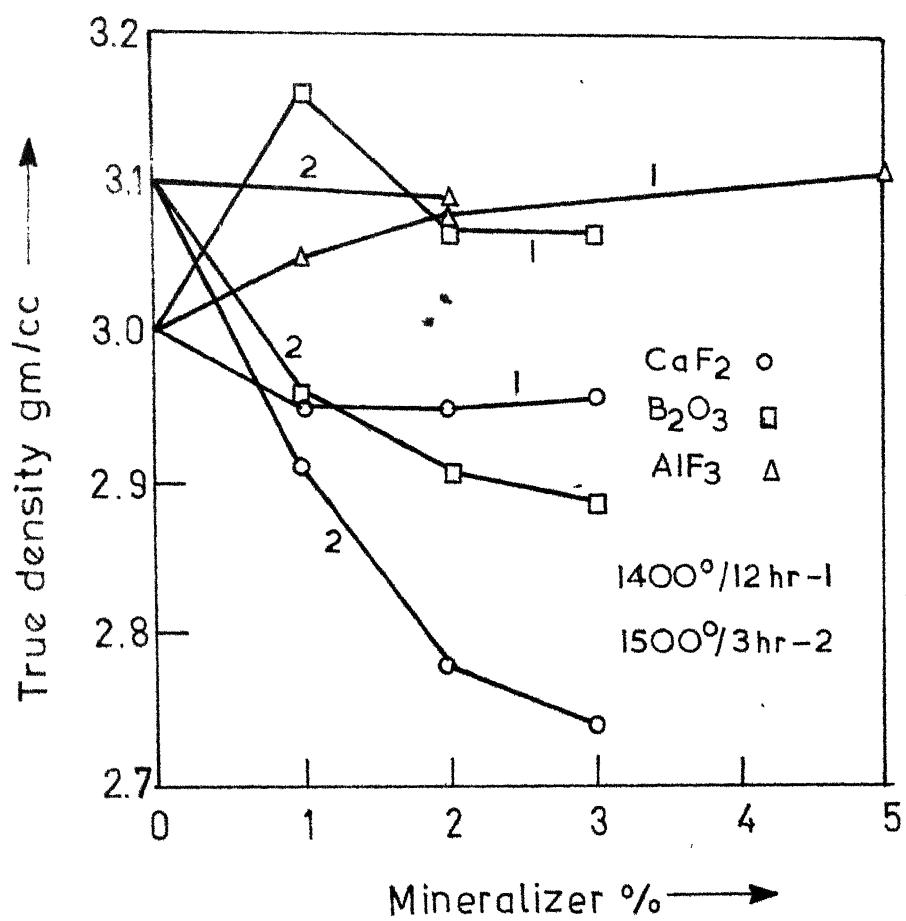


Fig. 4.6b Mineralizer vs density.

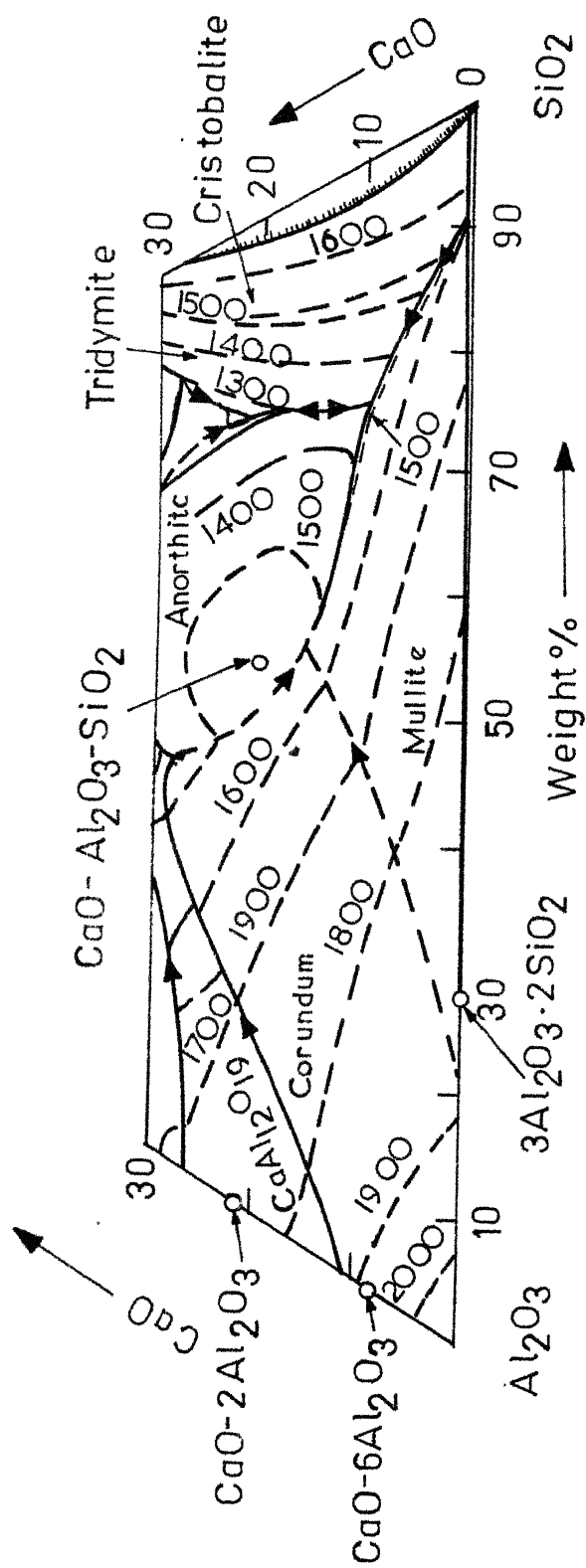


Fig.4.7 Part of the system $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$

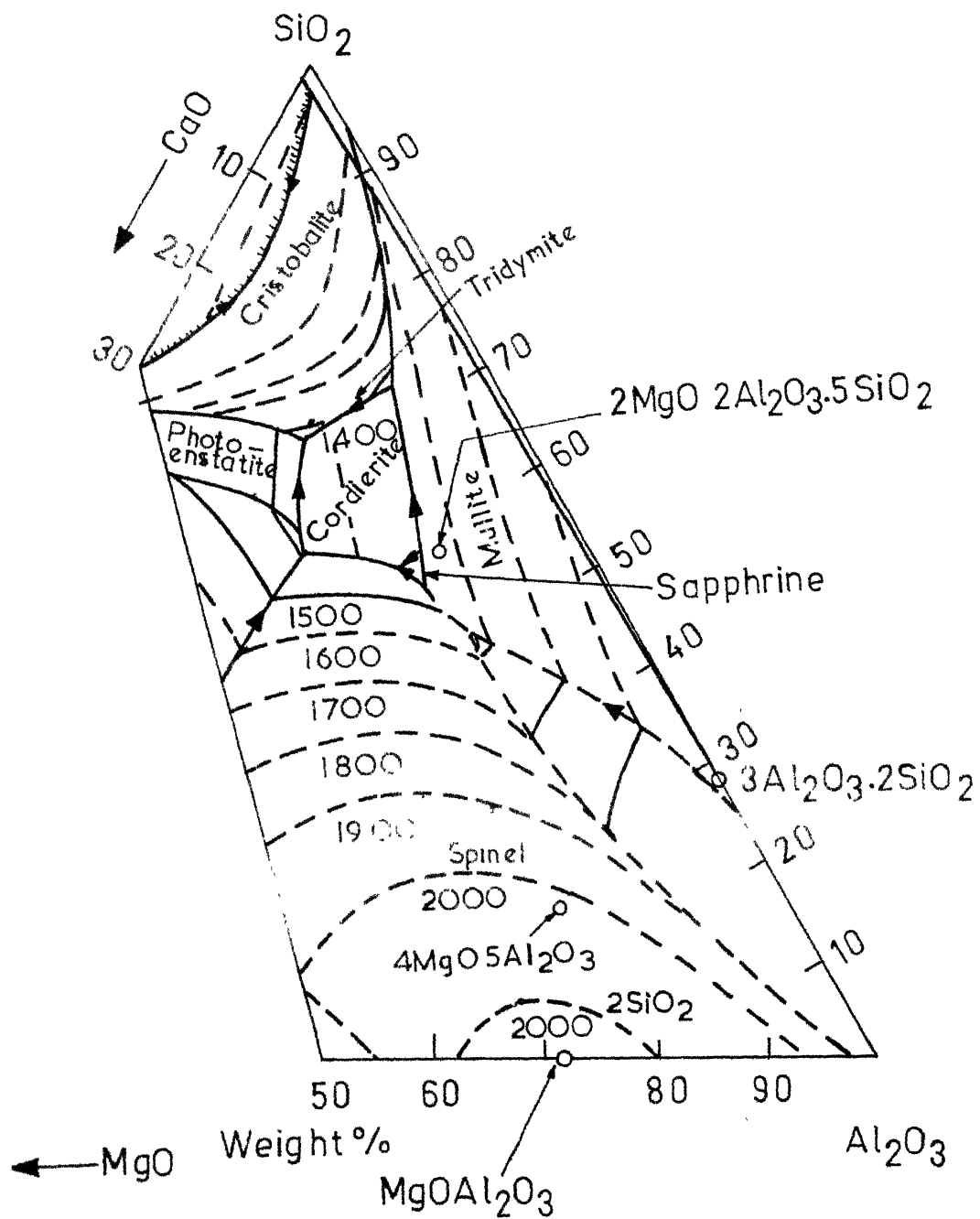


Fig.4.8 Part of the phase diagram of the system $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$

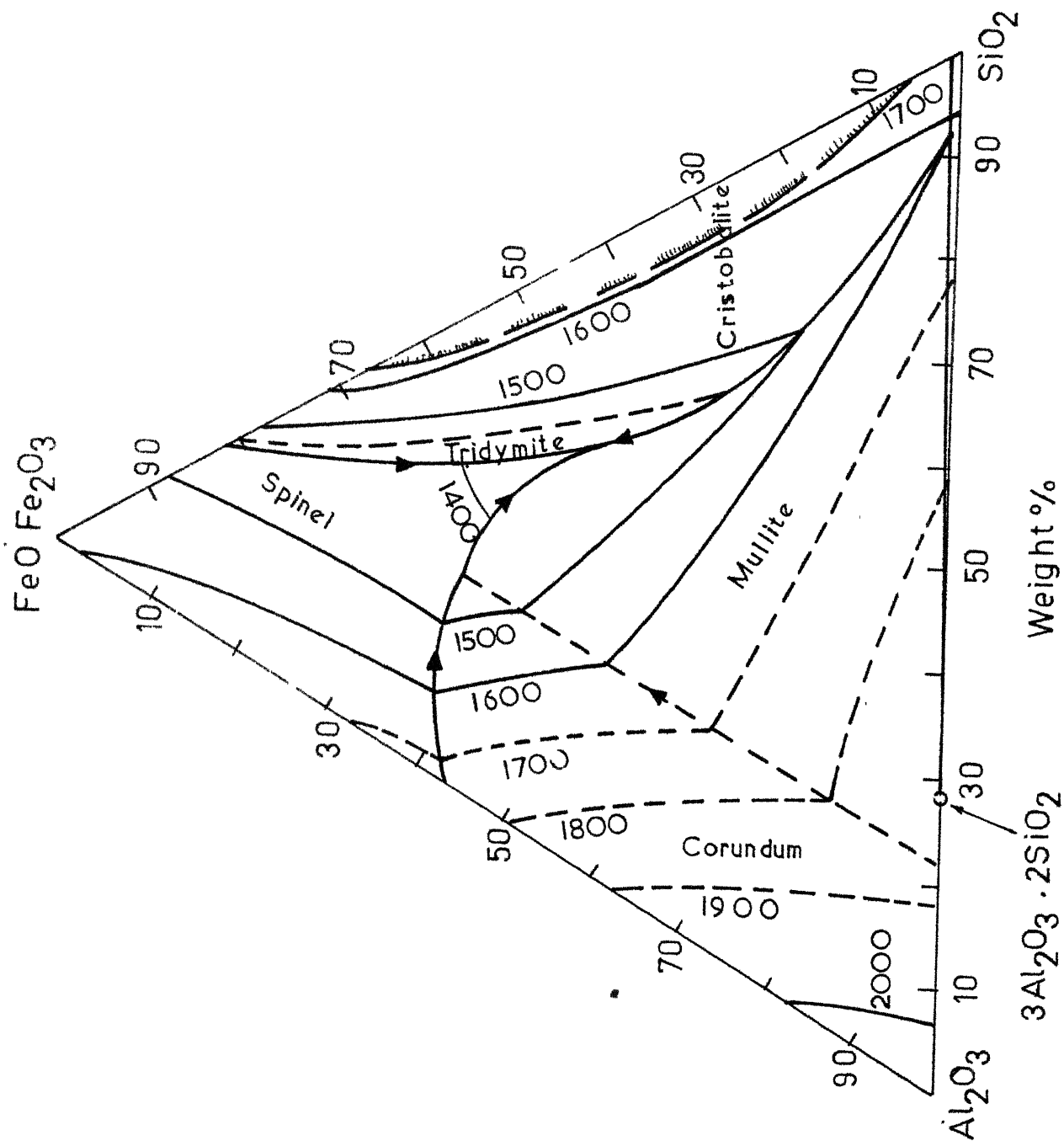
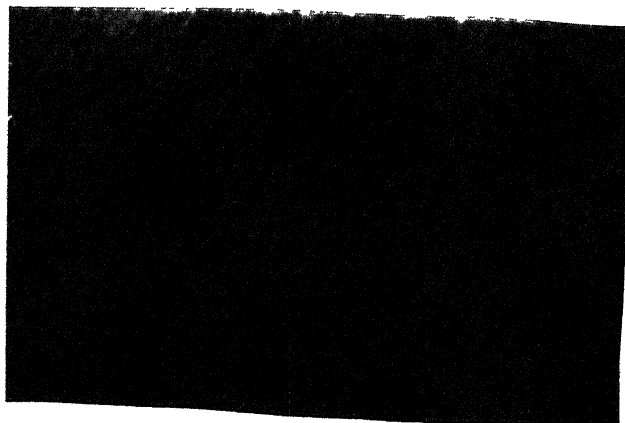


Fig. 4.9 Iron oxide - Al₂O₃ - SiO₂ in air. Phase relations at liquidus

1. 1α 1400' / 6 hr

55 CLAY
45 A=2 ; 300x



2. 1A: 1400' / 12 hr

55 CLAY
45 A=2 ; 300x



3. Cu CuO = 2.5:1.
 SSCLAY
 45A=2 ; 1400°/6hr



4. CuA ; CuO = 0.5:1.
 SSCLAY
 45A=2 - 1400°/12h ; 300X



5. CuC CuO = 1.5:1.
 SSCLAY
 45A=2 1400°/12h 300X



6. CuE ; CuO = 2.5:1.
 SSCLAY
 45A=2 ; 1400°/12hr ; 300X



7. MnA $MnO_2 = 0.5\%$
55CLAY; $1400^\circ/12h$; $300\times$
 ASA=2



8. Zn; $ZnO = 1.0\%$
55CLAY; $1400^\circ/6hr$
 ASA=2



9. ZnB; $ZnO = 1.0\%$
55CLAY; $1400^\circ/12h$; $300\times$
 ASA=2

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

The main conclusions that can be drawn from the present work are:

- (1) While temperatures of 1600°C and above are needed for the formation of sintered mullite from clay alumina mixtures, the temperature can be lowered to $1400\text{--}1500^{\circ}\text{C}$ by the addition of about 1 percent of mineralizers without significantly affecting the properties of the final product.
- (2) The mineralizers may be arranged in the decreasing order of effectiveness as CuO , Fe_2O_3 , ZnO , MnO_2 , CaO and MgO . It must however be noted that the differences in the effectiveness of these is not great. If whiteness of the sintered mullite is a requirement, transition metal oxides such as CuO and MnO_2 should be avoided as mineralizers.
- (3) The optimum amount of a mineralizer is a function of sintering conditions.
-) Malco alumina is nearly as good a source of alumina as Alcoa A = 2.

- (5) The fact that fine grained Alcoa A = 16 and Hydral 710 improve mullitization, super grinding of Malco alumina should be beneficial.
- (6) Under the conditions of the present investigation, it was found necessary to decrease alumina content in the mix to below the ideal mullite composition in order to obtain maximum mullite. This was attributed to the vapourization of SiO_2 during sintering. The optimum ratio of clay/alumina was found to be 57/43.

The present work paves the way for large scale industrial trials of producing sintered mullite. In this connection the following recommendations are made.

- (1) Large batches of the clay alumina mixes may be produced with $A = 2$ and super ground Malco alumina as sources of alumina with and without appropriate mineralizers.
- (2) Clay and alumina may be ball milled together for more intimate mixing.
- (3) More detailed microstructural studies may be useful to relate the shape and size of mullite crystals with processing parameters.

- (4) Better particle size control of the starting materials is essential to decrease porosity from the present level of 20-30 percent to values which can be tolerated in electronic applications of mullite and in crucibles etc.

REFERENCES

1. Shepherd E.S.; Rankin, G.A.; Wright. W.: Amer. J. Sci. 28, 301, 1909 (Chem. Abs. 3, 2925).
2. Shepherd E.S., Rankin G.A., Wright F.E.: Z. Anor. Alleg. Chem. 71, 22, 1911. (Chem. Abs. 5, 1982).
3. Shepherd E.S., Rankin G.A., Wright F.E.: Amer. J. Sci. (4) 39, 1, 1915.
4. Bowen N.L. and Greig J.W.: J. Amer. Ceram. Soc. 7, 238, 410 (Chem. Abs. 18, 2587) 1924.
5. Morris L.D., Shore S.R.: J. Amer. Ceram. Soc. 18, 359, 1935. (Chem. Abs. 30, 258²).
6. Bauer W.H., Gordon I., Moore C.H.: J. Amer. Ceram. Soc. 33, 140, 1950.
7. Toropov N.A., Galakhov, F.Ya.: Izv. Akad. Nauk. SSSR Otd. Khim. Nauk. 78, 299, 1951 (Chem. Abs. 49, 2845d, 12802d).
8. **Budnikov P.P., Tresryatski S.G., Kushakovski V.J.:** Dokl. Akad. Nauk. SSSR 93, 291, 1953 (Chem. Abs. 50, 3864e).
9. Eilonenko N.E. and Lavrov I.V.: Dokl. Akad. Nauk. SSSR 89, 141, 1953 (Chem. Abs. 50, 2938g).
10. Posnjak E. and Greig J.W.: J. Amer. Ceram. Soc. 16, 569, 1933 (Chem. Abs. 28, 275²).

11. Sosman R.B.: J. Amer. Ceram. Soc. 16, 60, 1933
(Chem. Abs. 27, 823; 29, 3902⁴).
12. Rooksby H.B., Partridge J.H.: J. Soc. Glass Tech.
23, 338T, 1939.
13. Barta R. and Barta Ch.: Zh. Priklad. Khim. 29, 341,
1956 (Chem. Abs. 50, 1419c).
14. Neuhaus A. and Richartz W.: Ber. Deut. Keram.
Ges. 35, 108, 1958 (Chem. Abs. 54, 6280g).
15. Shears E.C. and Archibald W.A.: Iron Steel (London)
27, 26, 1954.
16. Trömel G.: Conference on Physical Chemistry of
Iron and Steelmaking, pp 77-78, M.I.T. Press,
Cambridge, Mass.
17. Toropov N.A. and Galakhov F.Ta.: Bull. Acad. Sci.
USSR Div. of Chem. Science 1958, 8.
18. Welch J.: Nature, 186, 545, 1960.
19. Aramaki S. and Roy R.: J. Amer. Ceram. Soc., 45,
229, 1962.
20. Horibe T. and Kuwabara S.: Bull. Chem. Soc. Japan,
40, 972, 1967.
21. Reyweld and Schiete : Ber. Deut. Ker. Ges., 48(6),
258-61, 1971 (Chem. Abs. 1, 24G, 1972).
22. Pask J.A. and Aksay I.A.: Science 183, 70, 1974.
23. Agrell and Smith : J. Am. Ceram. Soc. 43, 59, 1960.

24. Burnham C.W.: Yearb. Carnegie Inst. 61, 135, 1962
(Chem. Abs. 58, 8478e).
25. Sadanage R., Takonami M.: Takeuchi Y.: Acta Cryst.
15, 65, 1962.
26. Durovic S.: J. Amer. Ceram. Soc. 45, 157, 1962.
27. Burnham C.W.: Yearb. Carnegie Inst. 62, 158
(Chem. Abs. 59, 5880c; 60, 7532b); 63, 223, 227
(Chem. Abs. 62, 11243b).
28. Norton J.T.: J. Amer. Ceram. Soc. 8, 401, 1925;
ibid, 636 (Chem. Abs. 19, 3154).
29. Greig J.W.: J. Amer. Ceram. Soc. 8, 465, 1925
(Chem. Abs. 19, 3154).
- 29a. Peck A.B.: J. Amer. Ceram. Soc. 8, 407, 1925
(Chem. Abs. 19, 3154).
30. Miyashiro A.: J. Geol. Soc. Japan 55, 218, 1949
(Chem. Abs. 45, 841a).
31. Keyser W.L.: Bull. Soc. Franc. Ceram. 35, 9, 1957
(Chem. Abs. 53, 22803i).
32. Wilson H.H.: Amer. Ceram. Soc. Bull. 48(8), 796,
1969
33. Roy R., Roy D.M., Francis E.E.: J. Amer. Ceram.
Soc. 38, 198, 1955.
34. Comer J.J.: J. Am. Ceram. Soc. 44, 561, 1961.
35. Schielitz N.C. and Soliman M.R.: 13th Nat. Conf.
Clays Clay-Minerals Madison Wiscon 1964, 419.

36. Nicholson P.S.: J. Am. Ceram. Soc. 53, 2371, 1970.
37. Brindley G.W. and Nakahira M.: J. Am. Ceram. Soc., 42, 311, 1959.
38. Horte L.H. and Wilymann J.: Silikattech. 9, 358, 1958.
39. West R.R. and Gray T.J.: J. Am. Ceram. Soc. 41, 132, 1958.
40. Demediuk T. and Cole W.F.: Nature 181, 1400, 1958.
41. Goncharov X.O.: Dokl. Acad. Nauk. SSSR 105, 323, 1955 (Chem. Abs. 50, 8985a).
42. Neuhaus A.: Keram. Z. 9, 438, 1957.
43. Wahl F.M., Grim R.E., Graf R.B.: Am. Mineralogist 46, 1064, 1961.
44. Pankratz L.B., Weller W.W., Kelley K.K.: U.S. Bur. Mines. Rept. Invest. 6287.
45. Feusternacher J.E. and Hummel F.A.: J. Am. Ceram. Soc. 44, 284, 1961.
46. Lohre W. and Urban H.: Ber. Deut. Keram. Ges. 37, 249, 1960.
47. Williams J.C., Sinclair W.R., Koonce S.E.: J. Am. Ceram. Soc. 46, 161, 1963.
48. Budnikov P.P. and Shrukler K.M.: Zh. Priklad Khim. 19, 1029, 1946 [J. Am. Cer. Soc. Abs. 31(3), 54, 1948].

49. Kroll E.B. and Polyboyarinov D.N.: Tr. Gos. Nauchn. Issled. [Inst. Stroit. Keram. 24, 105, 1964; (Chem. Abs. 63, 1566c)].
50. Locsei B.: Proc. Conf. Silicate Indus. 6th Budapest, 291, 1963 (Chem. Abs. 58, 2255b; 60, 5180a; 61, 6751f; 61, 6755b, 14323c; 65, 11939d; 67, 35988p; 68, 62341z; 69, 46364z).
51. Insley H. and Ewell R.H.: J. Res. Nat. Bur. Stds. 14, 615, 1935 (Chem. Abs. 29, 5005^P).
52. McAtee J.L. and Milligan W.O.: Texas J. Sci., 2, 200, 1950.
53. Grofcsik J. and Gago E.: Epitoanyag.
54. Roy R.: J. Am. Ceram. Soc. 39, 145, 1956.
55. Bidet J.P. and Jouenna C.A.: Bull. Soc. Fr. Ceram. 39, 43, 1958.
56. Otani S. and Kojima A.: Kogyo Kagaku Zasshi 67, 1509, 1965 (Chem. Abs. 62, 12483).
57. Crofts J.D. and Marshall W.W.: Trans. Brit. Ceram. Soc. 66, 121, 1967.
58. Ghate B.B., Hasselman D.P.H., Spriggs R.M.: Ceram. Bulletin 52(7), 670, 1973.
59. Yoshioka T. and Isomachu M.: J. Jap. Ceram. Ass. 38, 200, 705, 1930 (Chem. Abs. 26, 3348).
60. Kraner H.M.: J. Am. Ceram. Soc. 21, 360, 1938.
61. Nakai T. and Fukami Y.: J. Jap. Cer. Ass. 47, 225, 1939 (Chem. Abs. 34, 2551²).

62. Parnelco C.W. and Rodriguez L.R.: J. Am. Ceram. Soc. 25, 1, 1942.
63. Akiyama K. and Kadogawa T.: J. Jap. Cer. Abs. 26, 227, 1943.
64. Budnikov P.P. and Shmukler K.M.: Zh. Priklad. Khim. 19, 1029, 1946 [J. Am. Cer. Soc. Abs. 31(3), 54, 1948].
65. Palmeri V.R.: J. Soc. Glass Tech. 36, 25-28N, 1962.
66. Skinner K.G. et al: J. Am. Ceram. Soc. 36, 349, 1953.
67. Avugustinik A.I. et al: Zh. Priklad. Khim., 27, 782, 1954 (Chem. Abs. 49, 581d; 50, 6009a).
68. Moore H. and Prasad M.R.: J. Soc. Glass Tech. 39, 3145, 1955.
69. Nazarenko M.F., Sviridenko V.A.: Izv. Akad. Nauk. Kaz. SSR. Ser Gorn. Dela. Met. Stroit. Stroimater. 1956, 34.
70. Budnikov P.P. et al: Silicaty Okisly Khim. Vys. Temp. 1963, 233.
71. Chaudhri S.P.: Trans. Ind. Ceram. Soc. 28, 24, 1969.
72. Ao T.: J. Soc. Chem. Ind. Japan 36, 546, 1933 (Chem. Abs. 28, 598¹).
73. Osborn E.F.: J. Am. Ceram. Soc. 36, 147, 1953.
74. Grofcsik J. and Tamas F.: 'Mullite, Its Structure, Formation and Significance', Publishing House of Hungarian Academy of Sciences, Budapest, pp 112, 1961.

75. McKenzie K.J.D.: Tr. Brit. Ceram. Soc. 68(3), 196, 1969.
76. Franc H. Chung: Advances in X-ray Analysis 17, 106, 1973.
77. Joshi T. et al: Ind. Jour. App. Chem. 26, 53-115, 1963.

APPENDIX

PRELIMINARY SINTERING STUDIES ON ALUMINA

The sintering behaviour of Alcoa A = 2 alumina was studied by sintering at 1400°C for 12 hrs, 1500°C for 3 hrs and 1600°C for 2 hrs. The following were used as variables.

- (1) Grinding of A = 2 alumina
- (2) Partial replacement of A = 2 by Hydral 710
- (3) Gradual replacement of A = 2 alumina by Alcoa A = 16
- (4) Mineralizers: CaO, FeO, Clay, AlF_3 , MnO_2 , B_2O_3 , $\text{Al}_2(\text{SO}_4)_3$, TiO_2 and MgO. The amounts added varied from 0.25-5.0 percent (10-50 percent in the case of $\text{Al}_2(\text{SO}_4)_3$) depending on each mineralizer.

The procedures employed are the same as those employed for the study of mullite and therefore are not described here again. The details of the various compositions tried are tabulated in Table A.1.

Shrinkage, porosity, geometric density and true density values are listed in Table A.2 to A.4.

A.1 Grinding of $A = 2$ Alumina

The grinding of the $A = 2$ alumina has a positive effect on the sintering of alumina. From Tables A.2 to A.4 it is seen that there is an increase in shrinkage, geometric and true densities and a pronounced decrease in the porosity values. This shows that super grinding or grinding in vibromill or fluid energy mill should lead to further improvement.

A.2 Replacement of $A = 2$ by $A = 16$ Alumina

The $A = 2$ alumina as received was replaced by $A = 16$ alumina. The $A = 16$ content was increased in intervals of 10 percent upto 80 percent. 100 percent $A = 16$ alumina was also included for reference. At each temperature the shrinkage and geometric density generally increased with the $A = 16$ content while the porosity decreased. The improvement is evident from the following summary.

Temperature/Time	1400/12			1500/3			1600/2		
Alumina	Porosity	G.D.	T.D.	Porosity	G.D.	T.D.	Porosity	G.D.	T.D.
$A = 2$	41.3	2.62	3.63	38.16	2.66	3.68	23.7	3.10	3.8
50 percent $A=16$	32.86	2.70	3.76	23.5	2.69	3.79	14.31	3.32	3.8
100 percent $A=16$	11.13	2.94	3.79	1.849	3.48	3.82	1.53	3.79	3.8

It is clear from the above that even by partial replacement of $A = 2$ by $A = 16$, geometric density as high as 3.4 can be achieved at 1500°C . Addition of $A = 16$ to $A = 2$ ground even for 24 hrs should cause further improvement in the properties of sintered alumina.

A.3 Replacement of $A = 2$ Alumina by Hydral 710

The $A = 2$ alumina as received was partially replaced by Hydral 710 in intervals of 10 percent upto 80 percent. While there was some improvement in the sintering behaviour of $A = 2$ by the addition of Hydral it turned out to be a much poorer choice than $A = 16$. The porosities in general were much larger and the geometric densities were poorer when compositions with corresponding amounts of $A = 16$ and Hydral are compared. This must be attributed to the porosity caused by the dehydration of hydral and the need for phase transformation of the dehydrated product to $\alpha\text{-Al}_2\text{O}_3$.

A.4 Mineralizers

The most effective mineralizers at all temperatures was found to be titania. The densification increased with increasing titania in the range studied. It is possible that a larger amount of titania may also be soluble in Al_2O_3 leading to even greater densities.

This observation is consistent with data available in the literature. The only drawback of titania additions is a slight yellowish tinge on the samples.

The second best mineralizer was MnO_2 . There is a striking improvement in the properties between 1500 and 1600°C. At 1500°C MnO_2 bearing samples are not as good as many others. But between 1500 and 1600°C the porosity drops from 33-38 percent to 5-10 percent while the geometric density jumped up from 2.3-2.4 to 3.2-3.4 gm/cc. Again the main drawback is the pink colour imparted on to the samples.

The data on the others are presented in Tables A.2 to A.4.

The general conclusion that can be drawn from this work is that A = 2 alumina after grinding would give sintered specimens at 1500-1600°C with porosities less than 5 percent. If TiO_2 is used as a mineralizer the temperature can be somewhat reduced by prior grinding of A = 2 alumina. In the study on mullite a general observation was made that Malco alumina behaves similar to A = 2 alumina. It is therefore worthwhile to undertake development work on sintered alumina based on Malco alumina after adequate grinding and with appropriate mineralizers.

Table A.1: Details of the Various Alumina Compositions

		Sintered at		1400°C	1500°C	1600°C
		for hrs		12	3	2
Name	Details					
	A = 2	A = 16	Hydral 710	Mineralizer		
A	50 (as received)					
Al	50 (24 hrs grinding)					
A2	50 (48 hrs grinding)					
B	45	5	-			
BX	45	-	7.70			
C	40	10	-			
CX	40	-	15.4			
D	30	20	-			
DX	30	-	30.8			
E	25	25	-			
EX	25	-	38.5			
F	20	30	-			
FX	25	-	25.0			
G	10	40	-			
GX	10	-	40.0			
H	-	50	-			
F1	100	-	-	0.03	Fe ₂ O ₃	
F2	-	100	-	0.05	Fe ₂ O ₃	
N1	100	-	-	0.25	MnO ₂	
N2	100	-	-	0.50	MnC ₂	
O1	100	-	-	1.0		
O2	100	-	-	2.0	B ₂ O ₃	
CA1	100	-	-	0.5	CaO	as CaCO ₃
CA2	100	-	-	1.0	CaO	
S1	100	-	-	10		
S2	100	-	-	20		
S3	100	-	-	30		Al ₂ (SO ₄) ₃
S4	100	-	-	40		
S5	100	-	-	50		
M1	100	-	-	0.25		
M2	100	-	-	0.5	MgO	as MgCO ₃
M3	100	-	-	1.0		
T1	100	-	-	0.25		
T2	100	-	-	0.5		
T3	100	-	-	1.0	TiO ₂	
T4	100	-	-	2.0		
KL	100	-	-	1.0	Kaolin	
L1	100	-	-	1.0		AlF ₃
L2	100	-	-	2.0		

Table A.2: Physical Properties of Sintered Alumina

$D_0 = 2.662 \text{ cm}$ Sintered at 1400°C for 12 hrs.

Sample	Shrinkage percent	Porosity percent	Geometric Density gm/cc	True Density gm/cc
A	3.51	41.3	2.62	3.63
A1	3.78	36.8	2.78	3.65
A2	4.14	32.4	2.91	3.72
B	3.61	35.8	2.38	3.72
BX	3.68	35.4	2.27	3.61
C	4.28	34.39	2.22	3.58
CX	4.73	37.44	2.3	3.65
D	5.18	34.93	2.57	3.96
LX	7.29	42.97	2.01	3.70
E	6.46	32.86	2.70	3.76
EX	8.64	29.07	2.03	3.10
F	6.84	26.41	2.94	3.77
FX	7.21	42.12	2.01	3.78
G	9.47	20.65	3.01	3.96
H	13.97	11.13	2.94	3.79
CA1	0.83	41.3	2.07	3.69
CA2	0.15	45.4	1.79	3.75
F1	2.33	39.30	2.23	3.73
KL	3.01	39.20	2.2	3.94
F2	9.92	23.06	2.90	3.80
L1	3.61	37.70	2.35	3.76
L2	3.75	37.85	2.30	3.71
M1	1.58	40.38	2.15	3.73
M3	1.58	42.99	2.12	3.90
C1	3.01	32.04	2.17	3.39
C2	3.16	40.65	2.23	3.79
S1	1.95	37.80	2.27	3.77
S2	2.40	37.11	2.18	3.51
T1	9.54	22.12	2.89	3.77
T2	11.50	17.98	3.05	3.77
T3	13.15	12.94	3.14	3.70
T4	13.45	10.82	3.23	3.26

Table A.3: Physical Properties of the Sintered Alumina

 $D_0 = 2.662 \text{ cm}$;Sintered at 1500°C for 3 hrs.

Sample	Shrinkage percent	Porosity percent	Geometric Density gm/cc	True Density gm/cc
A1	5.82	38.6	2.46	3.68
A2	7.1	25.7	2.81	3.71
A3	9.64	23.4	2.94	3.84
B	6.01	32.59	2.50	3.75
BX	4.73	31.86	2.37	3.59
C	4.88	34.49	2.45	3.81
CX	3.01	41.58	2.13	3.70
D	5.33	31.02	2.59	3.79
DX	9.69		2.32	3.79
E	5.86	23.55	2.69	3.79
EX	8.87	43.41	2.04	3.64
F	7.21	22.78	2.92	3.83
FX	8.11	37.06	2.61	3.73
G	12.17	1.91	3.43	3.59
GX	12.85	29.72	1.90	3.02
H	13.85	1.85	3.48	3.82
F1	11.27	12.58	3.44	3.56
CA1	6.38	38.19	2.30	3.73
CA2	8.50	27.60	2.62	3.77
KL	6.54	30.06	2.53	3.78
M1	3.33	37.44	2.30	3.76
M2	6.83	17.33	2.61	2.96
M3	3.23	37.15	2.30	3.78
N1	2.78	38.38	2.28	3.77
N2	4.66	33.26	2.39	3.68
O1	3.31	28.91	2.21	3.42
O2	4.88	36.51	2.35	3.78
S1	5.33	29.54	2.46	3.76
S2	7.44	28.66	2.50	3.69
T1	10.74	23.18	2.90	3.81
T2	14.27	9.94	3.28	3.68
T3	15.48	6.65	3.40	3.69
T4	14.50	5.64		3.66

Table A.4: Physical Properties of the Sintered Alumina

$D_0 = 2.662$ cm; Sintered at 1600°C for 2 hrs.

Sample	Shrinkage percent	Porosity percent	Geometric Density gm/cc	True Density gm/cc
A1	13.21	23.70	3.10	3.84
A2	15.40	19.00	3.14	3.86
B	13.22	14.81	3.21	3.77
BX	13.45	13.74	3.16	3.66
CX	14.27	1.42	3.33	3.43
D	14.73	5.07	3.49	3.51
E	11.87	14.31	3.32	3.79
EX	10.16	18.35	2.90	3.72
F	11.87	7.66	3.46	3.75
FX	17.13	14.05	3.18	3.61
H	17.36	1.53	3.79	3.83
CA2	11.72	9.78	3.29	3.59
F1	14.05	10.59	3.02	3.69
F2	17.43	8.73	3.28	3.96
KL	12.99	13.80	3.16	3.72
L1	13.52	14.55	3.20	3.76
M1	13.00	9.83	3.20	3.61
M2	12.70	14.13	3.11	3.70
M3	11.72	16.73	2.95	3.68
N1	14.50	10.74	3.19	3.87
N2	15.18	5.90	3.39	3.77
O1	13.22	17.02	3.12	3.78
O2	13.07	19.12	2.96	3.77
S1	12.77	14.18	3.26	3.77
S2	12.85	14.76	3.04	3.63
T1	12.77	1.67	3.54	3.56
T2	14.80	3.98	3.47	3.59
T3	13.75	6.25	3.78	3.54

